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Degree of Conversion Contributes to Dentin Bonding Durability of Contemporary Universal Adhesives

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Clinical Relevance

The degree of conversion of contemporary universal adhesives positively correlates with the bond strength to dentin. The correlation is more marked after thermocycling, suggesting that a high degree of conversion is required for long-term dentin bonding durability.

SUMMARY

Purpose: The objectives of this study were to evaluate the micro-tensile bond strength (μTBS) of five contemporary universal adhesives to dentin after 24 hours and thermocycling (TC), to measure their degrees of conversion (DC) and to test the correlation between μTBS and DC.

Methods and Materials: Four commercially available universal adhesives, Prime&Bond universal (PBU), Ecosite Bond (EB), G-Premio Bond (GPB), and Clearfil Universal Bond Quick (UBQ), and one experimental adhesive, UBQ without an amide monomer (UBQ-A), were used in this study. For the μTBS test, midcoronal dentin of 50 human molars was exposed, ground using 600-grit SiC paper, and the adhesives were applied according to the manufacturers' instructions. After resin-composite buildup and 24-hour water storage, one-half of the specimens were subjected to 15,000 thermal cycles. The specimens were sectioned into beams and stressed in tension at a cross-head speed of 1 mm/min until failure. The DC of adhesives applied to dentin was evaluated using attenuated total reflectance Fourier-transform infrared spectroscopy immediately after light-curing. All data were statistically analyzed at a significance level of 0.05.

Results: The highest μTBSs were obtained with UBQ, UBQ-A, and PBU, which were not significantly different from each other both after 24 hours and TC. The μTBS of GPB was lower compared with the aforementioned adhesives, but significantly only after TC, and the lowest

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μTBSs were obtained with EB. TC did not affect the μTBSs of UBQ, UBQ-A, and PBU significantly, but a significant decrease was observed with GPB and EB. The highest DC was obtained with PBU and UBQ, followed by 2-hydroxyethyl methacrylate–rich adhesives UBQ-A and EB, which exhibited significantly lower DCs. The DC of GPB could not be determined because the reference peak at 1608 cm^{-1} was not detected in its spectra. A significant positive correlation was shown between μTBS and DC after 24 hours (r=0.716) and TC (r=0.856).

Conclusion: μTBS and DC were positively correlated, more markedly after TC, which suggests that DC may be an important factor for bond durability.

INTRODUCTION

The range of use of contemporary one-bottle one-step self-etch adhesives has become very wide. The so-called universal adhesives are applicable to various substrates in both self-etch and etch-and-rinse modes and offer dentists a choice in almost any clinical situation. However, all one-bottle adhesives are very complex blends of hydrophilic and hydrophobic monomers, water, and solvents. Consequently, drawbacks including inferior durability, excessive water sorption, increased nanoleakage, phase separation (in 2-hydroxyethyl methacrylate [HEMA]-poor or HEMA-free adhesives), and reduced shelf life are frequently reported.[1]

Given the great simplicity and variability of the use of universal adhesives, focus has been placed on overcoming these drawbacks. However, the inevitable hydrophilicity resulting from the presence of hydrophilic monomers and water remains a problem,[2,3] because water diffusion into the adhesive layer after polymerization may lead to hydrolytic degradation and thus lower durability.[4,5] The increased water sorption is mainly associated with the presence of HEMA,[6,7] but it cannot be simply eliminated, because of HEMA's positive effect on the wetting properties of the adhesives and the ability to prevent phase separation.[8] However, it is also reported that HEMA has negative effects on the mechanical properties, bond strengths, and polymerization of the adhesives.[8-10] Hence, some newly marketed adhesives partially or completely replace HEMA with acrylamide monomers, which are claimed to reduce the aforementioned drawbacks. Recent studies report that the acrylamides exhibit lower water sorption, higher bond strength,[11] and favorable durability while preventing phase separation.[12] Acrylamide monomers are also more hydrolytically stable, allowing for a longer shelf life.[13]

Besides HEMA, the polymerization of one-bottle adhesives may be adversely affected by remaining solvent[14,15] and water,[16] because their complete evaporation is clinically difficult.[17] As a consequence, one-step adhesives are associated with a lower degree of conversion (DC) compared with multistep adhesives, which usually include a solvent-free resin as the final step. The lower DC may result in higher permeability,[18,19] lower durability, and impaired mechanical properties[17,20,21] of the simplified adhesives. Therefore, HEMA-free adhesives were introduced, and solvents such as isopropanol or tert-butanol[22] and more efficient photoinitiators[23-25] have been incorporated in some of the products to improve DC.

Four recent commercially available universal adhesives and one experimental product were included in this study. The adhesives differed in the content of HEMA, the incorporation of acrylamide monomers, solvent type, and photoinitiating systems. Their micro-tensile bond strength (μTBS) to dentin was evaluated both after 24 hours and after thermocycling (TC), and the immediate DC was measured using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). The main objective of this study was to investigate whether μTBS is correlated with DC. The null hypothesis was that there is no significant correlation between the μTBS and the DC of universal adhesives.

METHODS AND MATERIALS

Universal adhesives, Prime&Bond universal (PBU; Dentsply DeTrey GmbH, Konstanz, Germany), Ecosite Bond (EB; DMG CPF GmbH, Hamburg, Germany), G-Premio Bond (GPB; GC Corp, Tokyo, Japan), and Clearfil Universal Bond Quick (UBQ; Kuraray Noritake Dental Inc, Tokyo, Japan), and an experimental version of UBQ without the amide monomer, which was replaced with HEMA (UBQ-A; Kuraray Noritake Dental Inc), were used in this study. Table 1 presents a detailed description of the adhesives' composition and application procedures.

Micro-tensile Bond Strength Test

Specimen Preparation—Fifty sound human third molars were used for μTBS testing. The teeth were stored in distilled water at 4°C and used within six months of extraction. Before bonding, midcoronal

Table 1: *Composition, Batch Number, and Application Procedure of Adhesive Systems*

Adhesive System (Manufacturer)	Composition (Batch Number)	pH	Application
Prime&Bond Universal (Dentsply DeTrey GmbH)	10-MDP, bisacrylamide monomers, PENTA, isopropanol, water, initiator, stabilizer (1703000839)	2.5	1. Apply to the entire dentin surface and agitate for 20 seconds 2. Air dry for six seconds with mild air pressure (0.2 MPa) 3. Light cure for 10 seconds
Ecosite Bond (DMG CPF GmbH)	10-MDP, dental resins, HEMA, ethanol, water, additives, catalysts (788410)	4.5	1. Apply to the entire dentin surface, rub for 10 seconds and leave for 20 seconds 2. Air dry for five seconds with mild air pressure (0.2 MPa) 3. Light cure for 10 seconds
G-Premio Bond (GC Corp)	4-MET, 10-MDP, MEPS, methacrylate monomer, acetone, water, TPO, silica (1806201)	1.5	1. Apply to the entire dentin surface and leave for 10 seconds 2. Air dry for five seconds with maximum air pressure (0.35 MPa) 3. Light cure for 10 seconds
Clearfil Universal Bond Quick (Kuraray Noritake Dental Inc)	10-MDP, Bis-GMA, HEMA, hydrophilic amide monomer, colloidal silica, ethanol, water, silane coupling agent, sodium fluoride, CQ (041807)	2.3	1. Apply to the entire dentin surface 2. Air-dry immediately for six seconds with mild air pressure (0.2 MPa) 3. Light cure for 10 seconds
Clearfil Universal Bond Quick without amide monomer (Kuraray Noritake Dental Inc)	10-MDP, Bis-GMA, HEMA, colloidal silica, ethanol, water, silane coupling agent, sodium fluoride, CQ (171117)	2.3	1. Apply to the entire dentin surface 2. Air-dry immediately for six seconds with mild air pressure (0.2 MPa) 3. Light cure for 10 seconds

Abbreviations: 10-MDP, 10-methacryloyloxydecyl dihydrogen phosphate; PENTA, dipentaerythritol pentacrylate monophosphate; HEMA, 2-hydroxyethyl methacrylate; 4-MET, 4-methacryloxyethyl trimellitic acid; MEPS, methacryloyloxyalkyl thiophosphate methylmethacrylate; TPO, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; Bis-GMA, bisphenol-A-glycidyl methacrylate; CQ, camphorquinone.

dentin surfaces were exposed using a low-speed diamond saw (Isomet 1000, Buehler, Lake Bluff, IL, USA) under water cooling and ground using a wet 600-grit SiC paper (DCCS, Sankyo Fuji Star, Saitama, Japan) to produce a standardized smear layer.

Adhesive Application—For each of the five adhesives, 10 teeth were randomly selected. First, the dentin surfaces were gently air-blown to remove excess water. Then, the adhesives were applied using a disposable microbrush and air-blown according to the respective manufacturer's instructions (Table 1). The adhesives were light-cured from a distance of approximately 2 mm for 10 seconds using an LED light curing unit (10 seconds, 1000 mWcm^{-2}, Valo, Ultradent Products Inc, South Jordan, UT, USA). Next, the teeth were built up using resin composite Clearfil AP-X (shade A2, Kuraray Noritake Dental Inc) to a thickness of approximately 5 mm. The buildups were constructed in three increments less than 2 mm in thickness, and each of them was light-cured for 20 seconds (1000 mWcm^{-2}, Valo, Ultradent Products Inc). All the procedures were performed under standard room conditions, 23°C, and a constant relative humidity. The specimens were then stored in distilled water at 37°C for 24 hours.

Thermocycling—After 24-hour water storage, one-half of the specimens of each group (n=5) were subjected to 15,000 thermal cycles in distilled water at temperatures of 5°C and 55°C. The dwell time was 30 seconds and the transfer time was five seconds.

μTBS Testing—The specimens were sectioned perpendicular to the bonding layer into 12-16 non-trimmed beams using an Isomet saw (Isomet 1000, Buehler) under water cooling. The beams were approximately 1 × 1 × 8 mm in size, and their dimensions were checked using a digital caliper Mitutoyo CD15 (Mitutoyo, Kawasaki, Japan) for precise bonding area calculation. Using command-set glue (Model Repair II Blue, Dentsply-Sankin, Tokyo, Japan), the beams were attached to a flat μTBS jig and stressed at a crosshead speed of 1 mm/min until fracture, using an EZ Test testing machine (Shimadzu Corp, Kyoto, Japan). The μTBS in MPa was obtained by dividing the recorded force at failure by the calculated bonded area of the specimens.

Scanning Electron Microscopy (SEM) Analysis—The fractured specimens were mounted on brass stubs, dried, sputter-coated with gold, and observed using a scanning electron microscope (JSM-IT100, JEOL Ltd, Tokyo, Japan). Three different failure modes were distinguished: 1) adhesive failure (more than 80% of the failure within the adhesive or at the dentin-adhesive interface), 2) cohesive failure within substrates (more than 80% of the failure in dentin or resin composite), and 3) mixed failure (the combination of adhesive and cohesive failure).

Statistical Analysis—Pretesting failures were considered left-censored data and were assigned a mean value between zero and the lowest μTBS measured in the respective group. The mean μTBSs calculated for each tooth were used as statistical units and analyzed using a two-way analysis of variance (ANOVA; factors material and storage condition). A multiple Student's *t*-test with Bonferroni correction was used for pairwise comparisons at a significance level of 0.05 (SPSS Statistics 23.0, IBM Corp, Armonk, NY, USA).

Weibull analysis was performed using the Weibull R package for R distribution (R Foundation for Statistical Computing, Vienna, Austria). Weibull scale (characteristic strength) and shape (modulus) parameters were calculated using a maximum likelihood estimation analysis, and 95% confidence intervals were calculated based on Monte Carlo simulations. The groups were compared using the strength at a 10% probability of failure (P10).

Degree of Conversion Analysis

Specimen Preparation—An additional five sound human third molars were sectioned using the Isomet saw (Isomet 1000, Buehler) under water cooling to obtain four to six thin coronal dentin specimens per tooth, approximately 1 × 3 × 4 mm in size. Their surfaces were ground with a wet 600-grit SiC paper (DCCS, Sankyo Fuji Star) to produce a standardized smear layer.

ATR-FTIR Analysis—The absorption spectra of the adhesives were obtained from the region between 4000 and 400 cm^{-1} at a 2-cm^{-1} resolution using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Five dentin specimens were randomly selected for each adhesive. The adhesives were applied and air-blown according to their respective manufacturer's instructions (Table 1). The spectra were acquired first without light-curing, then, the adhesives were light-cured for 10 seconds (1000 $mWcm^{-2}$; Valo, Ultradent Products Inc) and their spectra were immediately recorded. All the procedures were performed under standard room conditions, 23°C, and a constant relative humidity.

DC Calculation—DC is calculated using the equation $DC = 1 - (R_{\text{cured}}/R_{\text{uncured}})$, where R represents the ratio between the absorbance peak of aliphatic C=C double bonds (around 1638 cm^{-1}) and a reference peak (internal standard) around 1608 cm^{-1} representing the aromatic double bonds.[26-28] The DC data were statistically analyzed using a one-way ANOVA and Tukey's *post hoc* test ($\alpha=0.05$; SPSS Statistics 23.0, IBM Corp).

Correlation Between μTBS and DC—The mean μTBS values of each tooth (five per group) and the DC measurements (five per group) were used for the analysis. The Pearson correlation coefficient was calculated separately for each storage condition (24 hours, TC), $\alpha=0.05$ (SPSS Statistics 23.0, IBM Corp).

RESULTS

μTBS

The results are summarized in Table 2. The two-way ANOVA revealed that both the material ($p<0.001$) and storage conditions ($p<0.001$) had a significant effect on the μTBS and that their interaction also was significant ($p<0.019$). The highest μTBS values were obtained with UBQ, followed by UBQ-A, PBU, GPB, and EB. It should be noted that the spread of the μTBS values acquired with EB was huge both after 24 hours and TC, resulting in high SD and low Weibull modulus (shape parameter).

After 24 hours, the outcomes of the statistical analyses differed slightly. P10 of EB was significantly lower than that of all the other adhesives, which did not differ among each other. ANOVA did not identify any significant difference between the μTBSs of EB and GPB ($p=1$), and it revealed that the μTBS of GPB was significantly lower than that of UBQ ($p=0.022$).

After TC, the same results were obtained with ANOVA and Weibull analysis. The bond strength of EB was significantly lower than that of GPB ($p=0.002$), whose mean μTBS and P10 were significantly lower compared with PB ($p=0.014$), UBQ-A ($p=0.001$), and UBQ ($p=0.001$). Compared with the 24-hour values, a significant decrease in bond strength was found for EB ($p<0.001$) and GPB ($p=0.024$) after TC.

SEM Analysis

The prevailing failure mode was adhesive (exemplary images are presented in Figure 1). In most groups, the fracture propagated partly through the adhesive resin and partly at the dentin-adhesive interface, as the adhesive layers were very thin. However, with EB, the failures occurred mainly at the dentin-adhesive interface. Round-shaped droplets were observed within the adhesive layer of GPB (Figure

Table 2: *Results of Microtensile Bond Strength Test and Failure Mode Analysis*

Storage Condition	Adhesive	Mean ± SD (MPa)[a]	Characteristic Strength (95% CI)	Modulus (95% CI)	P10 (95% CI)[b]	Failure Mode, A/C/M (%)[c]
24-Hour water storage	PBU	66.3 ± 4.1 BCa	71.4 (68.4-74.4)	5.7 (4.7-6.7)	48.1 (43.4-52.3) cd	34/38/28
	EB	53.1 ± 13.2 Aa	59.9 (55.5-64.5)	3.0 (2.5-3.5)	28.2 (23.3-32.9) b	50/22/28
	GPB	60.0 ± 3.7 ABa	64.7 (62.1-67.3)	5.4 (4.6-6.2)	42.6 (39.0-46.0) c	76/16/8
	UBQ	74.5 ± 6.0 Ca	81.2 (77.3-85.1)	4.9 (4.1-5.8)	51.3 (45.7-56.3) cd	42/34/24
	UBQ-A	72.3 ± 4.4 BCa	78.4 (74.9-81.9)	5.2 (4.3-6.0)	50.6 (45.6-55.2) cd	33/51/15
Thermocycling	PBU	65.3 ± 4.9 Fa	71.4 (68.3-74.6)	5.5 (4.5-6.5)	47.3 (42.5-51.7) cd	25/36/39
	EB	31.2 ± 14.3 Db	36.2 (31.8-41.1)	1.7 (1.4-2.0)	9.6 (7.0-12.5) a	75/8/18
	GPB	49.9 ± 4.2 Eb	55.2 (52.6-57.8)	4.9 (4.1-5.7)	34.7 (31.0-38.1)b	78/18/4
	UBQ	70.2 ± 5.1 Fa	76.3 (73.1-79.5)	5.6 (4.7-6.7)	51.2 (46.2-55.6) d	37/35/28
	UBQ-A	69.6 ± 4.2 Fa	75.2 (72.2-78.3)	5.6 (4.7-6.6)	50.4 (45.6-54.7) cd	43/34/23

[a] *The mean microtensile bond strengths and SDs were analyzed using a two-way ANOVA and multiple Student t-tests with Bonferroni correction. Same uppercase letters indicate no statistically significant differences between adhesives under the same storage condition; same lowercase letters indicate no statistically significant differences between the storage conditions.*

[b] *Same lowercase letters indicate no statistically significant differences between groups based on the results of Weibull analysis.*

[c] *A, adhesive failure; C, cohesive failure within substrates (dentin or composite); M, mixed failure.*

Abbreviations: PBU: Prime&Bond universal, EB: Ecosite Bond, GPB: G-Premio Bond, UBQ: Clearfil Universal Bond Quick, UBQ-A: Clearfil Universal Bond Quick without amide monomer.

1). Cohesive and mixed failures were more frequent with increasing bond strengths. In this study, only three pretesting failures occurred, all of them in the EB group after TC.

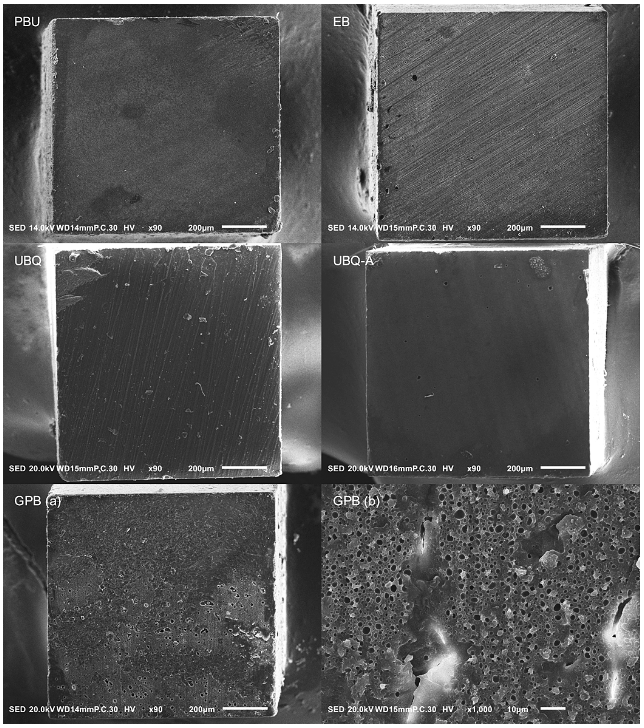


Figure 1. *Exemplary SEM images of each adhesive. The images show representative adhesive failures for each material at a 90× magnification. It can be noted that round-shaped droplets (1000× magnified in GPB [b]) were present within the layer of GPB, presumably resulting from the phase separation of its components. Abbreviations: PBU: Prime&Bond universal, EB: Ecosite Bond, UBQ: Clearfil Universal Bond Quick, UBQ-A: Clearfil Universal Bond Quick without amide monomer, GPB: G-Premio Bond.*

DC

DC in percentage is summarized in Table 3, and comparisons of spectra without and with light-curing for each material are presented in Figure 2. The highest DCs were obtained with PBU and UBQ, which were statistically similar ($p=0.842$). UBQ-A exhibited a DC significantly lower than PBU ($p=0.005$) and UBQ ($p=0.024$) but significantly higher than EB ($p<0.001$). GPB could not be evaluated because the peak at 1608 cm^{-1} was not detectable (Figure 2). Therefore, the correlations with μTBS were calculated only based on the results of PBU, EB, UBQ, and UBQ-A. A moderate positive correlation was revealed between DC and 24-hour μTBS ($r=0.716$), and a strong positive correlation was observed between DC and μTBS after TC ($r=0.856$). Both the correlations were statistically significant ($p<0.001$). The correlation graphs are presented in Figure 3.

DISCUSSION

New adhesives are frequently introduced to the market, often with spectacular claims regarding their properties. In this study, four recently commercialized universal adhesives and one experimental product were examined using a μTBS test and ATR-FTIR. The null hypothesis that there is no significant correlation between the μTBS and the DC of universal adhesives had to be rejected, because a significant correlation was revealed between DC and μTBS both after 24 hours and TC (Figure 3).

In this study, the DC of adhesives was evaluated after their application to dentin because it was

Table 3: *Degree of Conversion (Mean ± SD)*[a]

Adhesive	Mean ± SD (%)
PBU	75.5 ± 2.8 c
EB	31.3 ± 9.1 a
GPB	—
UBQ	72.8 ± 7.8 c
UBQ-A	61.2 ± 5.2 b

[a] *Same lowercase letters indicate no statistically significant differences between the adhesives' degree of conversion in percentages. The degree of conversion of GPB could not be determined because the reference peak at 1608 cm^{-1} was not detected.*

Abbreviations: PBU: Prime&Bond universal, EB: Ecosite Bond, GPB: G-Premio Bond, UBQ: Clearfil Universal Bond Quick, UBQ-A: Clearfil Universal Bond Quick without amide monomer.

previously reported that the DC of experimental functional monomer–containing adhesives improved in the presence of hydroxyapatite.[29] Because the aim of this study was to examine the correlation between DC and μTBS, we considered it essential to simulate the μTBS experimental settings (and the clinical situation), where functional monomers can interact with the hydroxyapatite of hard dental tissues. Due to the low penetration depth of mid-range FTIR (about 1-3 μm[30]), the underlying dentin did not seem to interfere with the adhesives' spectra despite the thin adhesive layers of one-step adhesives.

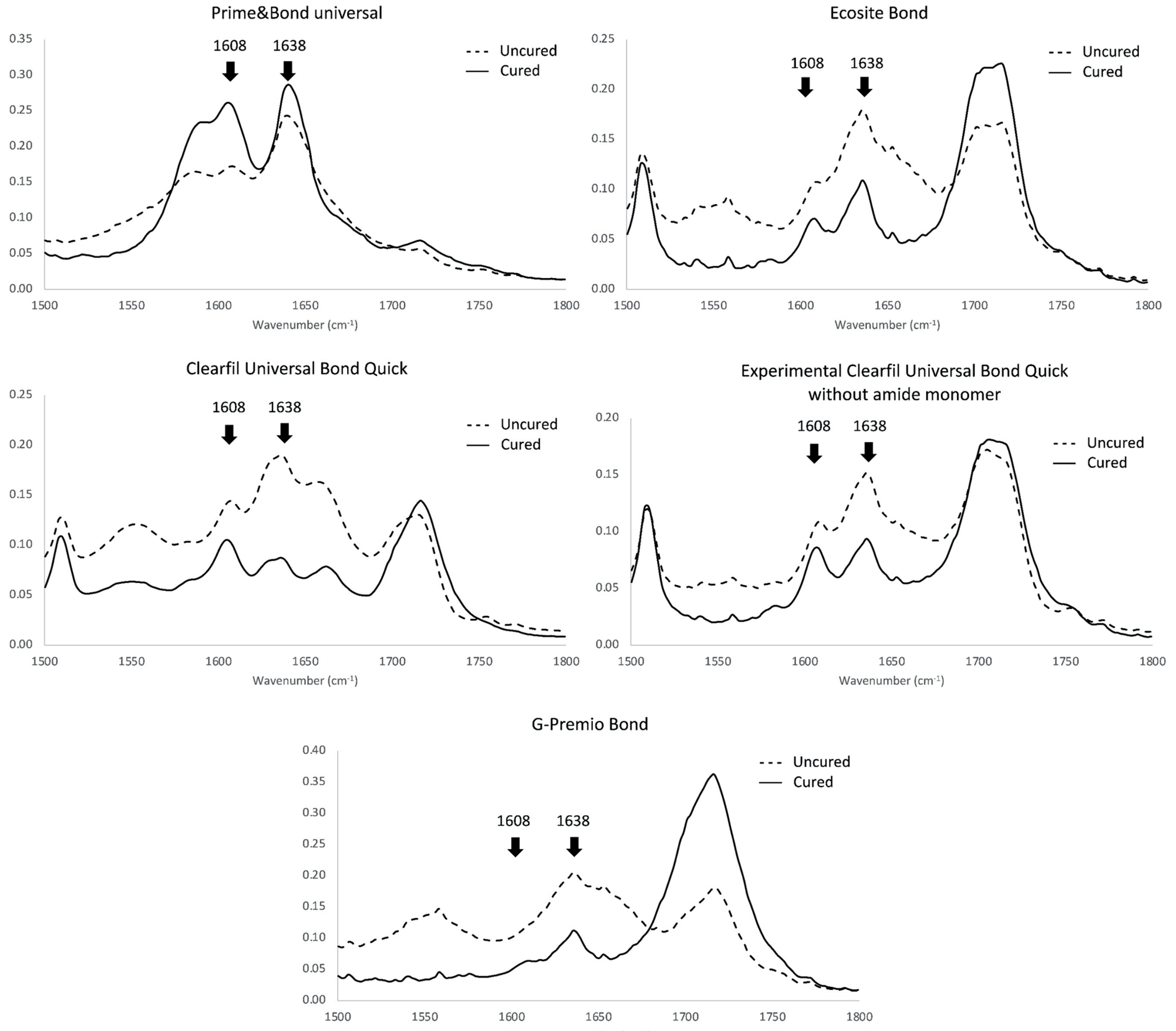
On the other hand, the chemical properties of the adhesives may change after the application to dentin. This was probably the case of GPB, where the 1608 cm^{-1} peak was successfully detected in previous studies when GPB was applied directly to the ATR crystal[27,28] but not when it was applied to dentin[27] (Figure 2). Given that the 1608 cm^{-1} peak represents aromatic carbon double bonds and that GPB does not contain bisphenol-A-glycidyl methacrylate (Bis-GMA), the only aromatic monomer that could be detected was 4-methacryloxyethyl trimellitic acid (4-MET). However, it is an acidic functional monomer and its conformation may change after the reaction of the carboxylic groups with hydroxyapatite, thus affecting the FTIR spectrum.

In some previous studies, the urethane (amide II) reference peak at 1538 cm^{-1} was used for Bis-GMA–free adhesives,[26,31] but it was not applicable in this study because the peak was not detected in all the adhesives. On the other hand, the carbonyl (C=O) peak at 1716 cm^{-1} was detectable in all the materials tested, and it had been used as an internal standard for simplified adhesives in a previous study.[26] However, some FTIR studies reported that the vibrations of vinyl and carbonyl groups are not independent[32,33] and that their conjugation is lost on polymerization.[33] Consequently, it was concluded that the peak could not be used as an internal standard.[33] Therefore, only the peak at 1608 cm^{-1} was used as the internal standard in this study, and the DC of GPB was not determined.

For the aforementioned reasons, the correlation between μTBS and DC was examined only based on the results of PBU, EB, UBQ, and UBQ-A. A significant positive correlation was revealed both after 24 hours and TC, but it was stronger after TC, which indicates that DC may be an important factor in long-term bond strength stability. Besides that, the results showed that the DC of adhesives with reduced HEMA content (PBU, UBQ) was significantly higher compared with HEMA-rich materials (EB, UBQ-A). This may be due to the hydrophilicity of HEMA, because the water retained in the adhesive may lead to reduced polymerization.[8] The presence of water in EB and UBQ-A was also confirmed by FTIR analysis, where the carbonyl peak at 1715 cm^{-1} was not sharp and symmetric, presumably due to hydrogen bonding of water, which shifts the peak to ~1700 cm^{-1} (Figure 2).[32]

UBQ exhibited the highest μTBS both after 24 hours and TC. UBQ is a fluoride-releasing 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP)–based HEMA-containing adhesive. However, the content of HEMA was reduced by the incorporation of a new hydrophilic amide monomer, and it has been claimed that no waiting time is necessary prior to light-curing. Although the μTBS obtained using the no-waiting approach was high, no significant difference from UBQ-A was found, which suggests that the incorporation of the amide monomer might not be the key feature. This is in contrast with a previous work where similar bond strengths of UBQ were obtained, but significantly lower μTBS was acquired for UBQ-A.[11] We speculate that the different outcomes could be caused by differences in the application procedure, such as the presence/absence of scrubbing or slightly variable application time. Shorter application times were reported to compromise the bonding performance of universal adhesives,[34] especially on diamond-bur-cut dentin where a thicker and more compact smear layer is present.[35,36]

Despite the addition of the new amide monomer, a previous study reported lower μTBS of UBQ to bur-cut dentin and an improvement of its bond strength after phosphoric-acid etching, which suggests that the penetration in self-etch mode was insufficient due to the presence of a thicker smear layer.[12] It is also noteworthy that the μTBS of UBQ was lower than that of Prime&Bond Active (Dentsply DeTrey



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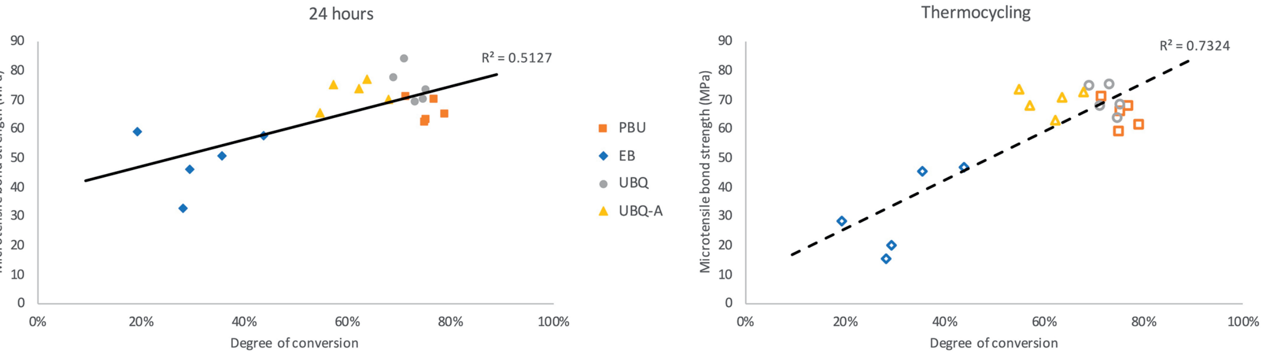

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Figure 2. *FTIR spectra of the adhesives (1500-1800 cm^{-1}). Comparison of the spectra before light-curing (dashed line) and immediately after light-curing (continuous line). The highlighted peaks at 1608 cm^{-1} (representing aromatic C=C double bonds) and at 1638 cm^{-1} (representing the aliphatic C=C double bonds) were used for the calculation of the degree of conversion. The peak at 1608 cm^{-1} is missing in the spectra of GPB, which is why its degree of conversion could not be calculated.*

GmbH),[12] which is (based on the available information) probably another brand name for PBU used in this study. This may indicate that the prolonged application time (20 seconds with agitation for PBU) could be beneficial for UBQ. Although Kuno and others did not observe any significant benefits from increased application time on SiC paper–ground dentin, the authors suggested that the effect could be significant on bur-cut dentin.[11]

Despite the arguable effect on application time, the presence of the amide monomer may bring more important advantages than saving a few seconds, such as improved DC and mechanical properties, higher durability, and lower water sorption. In this study, the DC of UBQ was significantly higher than that of UBQ-A, which could be due to its lower hydrophilicity compared with UBQ-A.[37,38] The durability of UBQ was also favorable; TC did not significantly reduce the bond strengths of UBQ in this study and the study of Ahmed and others.[12] Furthermore, higher ultimate tensile strength after water storage and lower water sorption were reported for UBQ,[11] which can also be attributed to the reduced content of HEMA. Last, acrylamide monomers are more hydrolytically stable and were reported to improve shelf life.[13,39]

PBU is another 10-MDP–based universal adhesive that features an acrylamide monomer, but unlike UBQ, HEMA is completely replaced. The DC of PBU was not significantly different from that of UBQ; both of them were significantly higher than the DC of HEMA-rich UBQ-A and EB. Slightly lower bond strengths were obtained with PBU compared with UBQ and UBQ-A; however, the difference was significant neither after 24 hours nor TC. No decrease in μTBS was noted for PBU after TC in this study, similar to a previous report of no significant effect of 50,000 thermal cycles on the μTBS of Prime&Bond Active.[12]

The durability of PBU may be attributed to lower hydrophilicity, resulting from the absence of HEMA, and to its DC. Given the longer application time[40] and the thin adhesive layer of PBU,[41] solvent evaporation could possibly be improved, resulting in increased DC[14,15] and lower adhesive permeability.[18,19] The solvent contained in PBU, isopropanol, was previously reported to be ineffective in the presence of HEMA[42]; however, PBU is a HEMA-free adhesive. Therefore, given the similar vapor pressure of isopropanol and ethanol,[22] they are likely to evaporate similarly. Last, the presence of PENTA (dipentaerythritol pentaacrylate monophosphate) could attribute to the DC, because its five double bonds make it an effective cross-linker.[43]

HEMA-free adhesives are usually prone to phase separation[44]; however, no droplets were observed within the adhesive layer of PBU using SEM (Figure 1). This is in accordance with the manufacturer's information, which claims that the bisacrylamide monomer is capable of keeping the hydrophobic monomers in solution, just like HEMA. In contrast to PBU, another HEMA-free universal adhesive, GPB, showed phase separation very clearly (Figure 1). Its bond strength was lower than those of PBU, UBQ-A, and UBQ, which is in agreement with a previous study, where GPB underperformed UBQ and Prime&Bond Active.[12] After 24 hours, the difference was significant compared with UBQ according to ANOVA, although not according to Weibull analysis. Both the analyses showed significant differences between GPB and all other adhesives after TC, which significantly reduced the μTBS of GPB. We speculate that lower durability of GPB may be attributed to the presence of 4-MET, which forms less stable calcium salts than 10-MDP[45] and is more susceptible to aging by TC.[46] The purity of 10-MDP was also proved to affect the bond strengths and stability on aging.[47]

Given the content of 4-MET, which is relatively hydrophobic due to its aromatic ring,[43] GPB is solvated by acetone. Acetone-based adhesives were reported to retain less water and solvents than ethanol-based ones,[38] which could favorably affect the DC of GPB. Moreover, GPB contains a diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide photoinitiator (known as TPO), which is very effective.[25] However, for the aforementioned reasons, the DC of GPB applied to dentin could not be evaluated in this study. In our previous study, where GPB was applied directly on the ATR crystal and the 1608 cm^{-1} peak was detected, its DC was 76.3 ± 3.9%, which is comparable to the results of PBU and UBQ in this study. In contrast, another recent study reported that the DC of GPB (67.2 ± 3.8%) was the

Figure 3. *Correlation graphs of micro-tensile bond strength and degree of conversion. Mean μTBSs of each tooth associated with DC values of PBU, EB, UBQ, and UBQ-A are shown in the scatter plot. GPB is not be included because its DC could not be determined. The continuous line visualizes the correlation of DC and μTBS after 24 hours and the dashed line after TC. It can be noted that the correlation after TC is stronger than after 24 hours. Abbreviations: PBU: Prime&Bond universal, EB: Ecosite Bond, UBQ: Clearfil Universal Bond Quick, UBQ-A: Clearfil Universal Bond Quick without amide monomer, μTBS: Micro tensile bond strength, DC: Degree of conversion.*

lowest among six universal adhesives,[27] but it must be noted that a light-curing unit emitting light only in the blue region (440-480 nm) was used in that study[27] and was ineffective for the activation of TPO[23-25] contained in GPB.

EB was included in the study because of its extremely low acidity (pH=4.5 according to the safety data sheet[48]), which is much milder than the other tested adhesives (Table 1). However, the manufacturer did not provide details about the composition except for the fact that it is 10-MDP based, which hinders the discussion. After 24 hours, ANOVA did not show any significant difference between EB and GPB, whereas Weibull analysis found the bond strength of EB to be significantly lower. The differences to other adhesives after 24 hours were significant according to both the statistical analyses. After TC, which decreased the μTBS of EB significantly, the bond strengths of EB were significantly lower compared with all other tested adhesives. The huge SD and low Weibull modulus of EB also imply its low reliability. Given the limited information, we assume that the pH was insufficient to interact with the smear layer and dentin, resulting in low bond strengths and failures at the dentin-adhesive interface. It must be noted that the insufficiency of EB's etching effect would be even more pronounced on bur-cut dentin.[35] The DC of EB was significantly lower than that of the other adhesives, which could also contribute to its low bond strengths.[20,21] The considerable decrease in the μTBS of EB after TC could be a consequence of increased water permeability due to low DC[18,19] and HEMA content.[48]

CONCLUSION

This study revealed that there is a significant positive correlation between μTBS and DC. The correlation was more marked after TC, which suggests that DC may be an important factor for long-term bond stability.

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Regulatory Statement

This study was conducted in accordance with all the provisions of the local human subjects oversight committee guidelines and policies of the Human Research Ethics Committee of Tokyo Medical and Dental University. The approval code issued for this study is 2014-022.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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