Original Article

Chemical stability of two dentin single-bottle adhesives as a function of solvent loss

Estabilidade química de dois adesivos dentinários de frasco único em função da perda de solvente

Ismael Yevenes[a]
Maria Olga Baltra[b]
Iván Urzua[b]
Juan Reyes[a]
Ljubica Petrasic[b]

[a] Department of Chemistry, Faculty of Dentistry, University of Chile, Santiago, Chile
[b] Department of Operative Dentistry, Faculty of Dentistry, University of Chile, Santiago, Chile

Abstract

Purpose: Two single-bottle dentin adhesive systems, Single-Bond and Prime and Bond NT, containing ethanol-water or acetone as solvents, respectively, were investigated for their chemical stability regarding solvent loss.

Methods: Stability was measured by the adhesive weight changes in accelerated degradation tests under higher room temperature and relative humidity (RH) than normal conditions over 15 days: 25±2°C / 60±5% RH, 30±2°C / 65±5% RH, 40±2°C / 70±5% RH, and 50±2°C / 75±5% RH. For each temperature the slope and the constant rate for weight loss were recorded to obtain the Arrhenius plot. Water content in Single Bond was determined by K Fisher Titration, and total solvent amount was obtained by subtraction from total weight.

Results: The results for Single Bond indicated water content of 5.90±0.08% and alcohol content of 39.14±1.19%. For Prime and Bond NT the acetone percentage was 43.08±1.15%. Weight changes after the accelerated degradation tests revealed that solvent loss in Single-Bond adhesive was lower than in Prime and Bond NT adhesive.

Conclusion: The results suggest that chemical stability of adhesives containing ethanol-water is greater than formulations containing acetone.

Key words: Stability; solvent; dentin adhesive

Resumo

Objetivo: Dois sistemas adesivos de frasco único, Single-Bond e Prime and Bond NT, contendo etanol-água e acetona como solventes, respectivamente, foram avaliados quanto à sua estabilidade química devido à perda de solvente.

Metodologia: A estabilidade foi medida pelas alterações de peso do adesivo em ensaios de degradação acelerada sob condições de temperatura e umidade acima das condições normais ao longo de 15 dias: 25±2°C / 60±5% RH, 30±2°C / 65±5% RH, 40±2°C / 70±5% RH, e 50±2°C / 75±5% RH. Para cada temperatura, a inclinação e a taxa constante de perda de peso foram registradas para obter o gráfico de Arrhenius. O conteúdo de água no adesivo Single Bond foi determinado por ensaio K Fisher e a quantidade total de solvente foi obtida pela diferença com o peso total.

Resultados: Os resultados para Single Bond indicaram conteúdo de 5,90±0,08% de água e 39,14±1,19%de álcool. Para Prime and Bond NT a porcentagem de acetona foi de 43,08±1,15%. As alterações de peso depois dos ensaios de degradação acelerada mostraram que a perda de solvente no adesivo Single-Bond foi menor que no adesivo Prime and Bond NT.

Conclusão: Os resultados sugerem que a estabilidade química do adesivo contendo etanol-água é maior que da formulação contendo acetona.

Palavras-chave: Estabilidade; solvente; adesivo dentinário

Correspondence:
Ismael Yevenes
University of Chile
Faculty of Dentistry, Department of Chemistry
Olivos 943, Independencia
Santiago – Chile
E-mail: iyevenes@odontologia.uchile.cl

Received: March 4, 2008
Accepted: June 11, 2008

Introduction

One-step dentin adhesives contain primer and bonding agents in a single bottle and were introduced in the market several years ago (1-3). They contain a combination of hydrophilic monomers, reactive diluent monomers, high viscosity adhesive resins, and photoinitiator systems, all provided in a single bottle solution containing ethanol or acetone as solvents. Some adhesives may include additives such as water, fillers, and fluoride-releasing agents in their composition (4). They are applied to wet, acid-conditioned dentin in single or multiple coats and light-cured separately before the restorative material is used. In contrast, multiple-step systems comprise one or more separate primers that should either be applied separately and sequentially to the acid-etched dental substrate, or should be mixed together immediately before using to prevent premature polymerization of adhesive components (5).

Micromechanical retention is considered the most important mechanism for bonding resin to dentin. Such retention only occurs when the resin completely infiltrates the demineralised dentin, creating a hybrid or resin-reinforced dentin layer in the superficial demineralised intertubular dentin matrix and resin tags within the dentin tubules (6). It is generally believed that the formation of a hybrid layer and resin tags depends on several factors, such as extension of acid-conditioning, post-etching moisture conditions of dentin surface, adhesive composition, and material diffusion into the exposed micro-porous collagen network (7). Moisture of dentin surface seems to be essential to achieve effective resin infiltration by the currently available single-bottle adhesives (8).

The presence of organic solvents in the formula of dentin adhesives is important because these dissolvents may affect the adhesion process. Water is crucial during the initial phase of dentin infiltration to maintain the structural integrity of the demineralised collagen fibrils. Water also keeps the interfibrilar spaces open so that the bonding resin can permeate these spaces because of the water-displacing capability of the volatile solvent in single-bottle adhesive systems (9). Also, adhesive stability depends on the content of organic solvent. The loss of solvents modifies the properties of multi-step adhesives and their effect on resin bonding to dentin. Therefore, determining adhesive stability with solvent loss would be important for proper handling and storage of these products in the daily clinics.

In the present work, two single-bottle dentin adhesives with different solvent bases were tested by measuring solvent loss. The chemical stability of the adhesive composition was monitored in accelerated degradation experiments by assessing weight changes. The amount of water was determined by K Fischer Titration, and the amount of total solvent was obtained by heating at a constant temperature until the weight was found constant.

Methodology

Two single-bottle dentin adhesive systems with different solvent bases were tested: Single Bond (3M ESPE, St Paul, MN, USA), an ethanol/water-based system; and Prime and Bond NT (Dentsply DeTrey, Konstanz, Germany), a water-free, acetone-based system. The adhesive chemical composition and pH values are displayed in Table 1.

Table 1. Composition of the two one-bottle dentin adhesive systems tested

Adhesive systems	Composition	Solvent
Single-Bond (SB)	Bis-GMA, HEMA, Dimethacrylates, polyalkenoic acid co-polymer, photoinitiators	Water, ethanol pH = 4.6
Prime and Bond NT (PB)	PENTA, UDMA, Resin R5-62-1, T-resin, D-resin, nanofillers, photoinitiators, stabilizercetylamine, hydrofluoride	Acetona pH = 2.1

Adhesive Stability

A total of 36 original containers of the two tested adhesives (Single Bond and Prime and Bond NT) were used in this study. Stability of the adhesive systems was determined relatively quickly by accelerating the degradation process with physical and chemical changes of the tested formulations. The stability experiment was carried out at higher room temperature and relative humidity (RH) than normal conditions: 25±2ºC / 60±5% RH, 30±2ºC / 65±5% RH, 40±2ºC / 70±5% RH, and 50±2ºC / 75±5% RH.

The adhesive bottles were opened and stored uncovered to be analyzed after 1, 3, 5, 7, 10, and 15 days by measuring weight changes. The stability study was carried out by storing three containers at 25ºC. The initial content was determined by mass measurements with a method that was developed in our laboratory based on standard stability methods. The percentage of mass remaining was plotted against time for each temperature. The slope of the regression line was obtained for each temperature, and the constant rate for weight loss was of zero-order. The logarithm of zero-order of the constant rate for loss of weight was plotted against the inverse of temperature in Kelvin degrees to obtain the Arrhenius plot. The experimental parameters were used to predict the speed of solvent loss under other temperature conditions. Data were analyzed by ANOVA and Tukey test at the 0.05 level of significance.

Determination of water content in Single Bond by K Fischer Titration

K Fischer titration is a widely used analytical method for quantifying water content in a variety of products (10): [12]

K Fischer Reaction

$$\mathrm{ROH + SO_2 + R'N} \rightarrow \mathrm{[R'NH]SO_3R + H_2O + I_2 + 2R'N} \rightarrow \mathrm{2[R'NH]I + R'NH]SO_4R}$$

The alcohol (ROH) reacts with sulphur dioxide (SO_2) and base (R'N) to form an intermediate alkylsulfite salt, which is then oxidized by iodine to an alkylsulfate salt. This oxidation reaction consumes water. Water and iodine are consumed in a 1:1 ratio in the above reaction. Once all water content is consumed, the presence of remaining iodine is detected voltametrically by the titrator indicator electrode. The signals of change in color indicate the titration endpoint. The amount of water present in the sample is calculated based on the concentration of iodine in the K Fisher titrating reagent (*i.e.*, titer) and the amount of K Fisher reagent consumed in the titration. Water content was determined for each temperature and time of incubation.

Determination of total solvent in Single Bond

Weight changes were measured when the specimens were heated at a constant temperature. These measurements provide quantitative parameters for specimen composition as water and other volatile components evaporate when the specimen is heated, and specimen weight decreases. Hydroquinone (0,0344g) was added, and the open bottles were incubated in a Thermolyne Dri-Bath Incubator (Barnstead International, Thermo Fisher Scientific Inc., Dubuque, IA, USA) at 80°C. The samples were weighed in analytical balance every 24 hours until constant weight was reached.

Results and Discussion

When a water-free, acetone-based adhesive system such as PB is applied, the acetone solvent can efficiently displace water from the dentin surface and moisten collagen network. Subsequently, the adhesive resin monomer can completely infiltrate into the subfibrillar space of the collagen network and provide excellent micromechanical interaction due to affinity between fibrils and resin (11). On the other hand, when a water-containing, ethanol-based adhesive system such as SB is used, the residual water remaining after ethanol solvent evaporation may interfere with the surface interaction between collagen fibrils and resin (12). Ethanol-water combination forms an azeotropic mixture and combines ethanol and water when evaporated, leaving less solvent in the adhesive.

Adhesive Stability at 25°C

The results of solvent loss at 25ºC after 1, 3, 7, and 15 days are shown in Fig. 1. At the beginning of the accelerated degradation tests, the amount of weight loss was similar and very low for both adhesives. Over the period of 15 days, weight loss gradually increased, and by the end of the second day weight loss become significantly different. The solvent content in Single-Bond adhesive always was larger than that in Prime and Bond NT adhesive. By day 15, solvent loss was 4.48% (wt) in Prime and Bond NT adhesive, but only 2.19% (wt) in Single-Bond adhesive. This suggests that the ethanol-water-based adhesive presents slower degradation than the tested acetone-based adhesive.

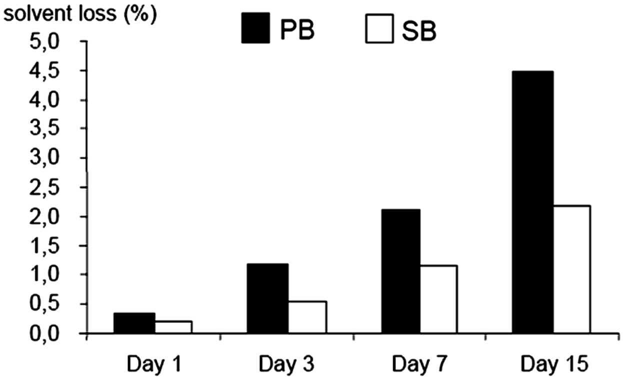

Fig. 1. Solvent loss (in weight; %) of the tested adhesives after accelerated degradation tests over 15 days. (SB: Single-Bond adhesive; PB: Prime and Bond NT adhesive).

Adhesive Stability after Accelerated Degradation

ANOVA for the speed (constant) of degradation at each temperature demonstrated significant differences ($P<0.05$) between the two adhesives. Furthermore, the degradation constant values were different for each temperature. Exposure of the tested adhesives to higher temperatures than 25ºC (30, 40, and 50ºC) allowed the determination of kinetics parameters of material degradation in each temperature (Table 2) to be used to plot the Arrhenius equation. These experimental parameters were used to predict the speed of degradation in others conditions (13).

Table 2. Constant of speed of mass loss (k) (in hours) for Single-Bond (SB) and Prime and Bond NT (PB) adhesives as a function of temperature

Temperature			Constant of speed of mass loss	
ºC	ºK	1/T	k (SB)	k (PB)
25	298	0.0034	- 0.0007	- 0.0010
30	303	0.0033	- 0.0014	- 0.0017
40	313	0.0032	- 0.0028	- 0.0034
50	323	0.0031	- 0.0060	- 0.0065

The kinetics of degradation shows a reaction of zero order. This implies that the speed whereupon the number of solvent molecules decreases is proportional to the number of molecules that remain intact, indicating that the parameter evaluated linear decay within time (14). From the regression line of the Arrhenius plot, the zero-order degradation constant at 20ºC was calculated to be 5.12×10^{-4} $hours^{-1}$ for Single-Bond adhesive and 9.12×10^{-4} $hours^{-1}$ for Prime and Bond NT adhesive. At room temperature, it was predicted that the products can lose 10% of mass after 8.46 days for Single-Bond adhesive and 4.75 days for Prime and Bond NT adhesive ($P<0.05$). Also the predictions for 50%

of solvent loss (shelf life) were different between adhesives: 56.4 days for Single-Bond and 31.7 days for Prime and Bond NT. The shelf life under refrigeration (4ºC) was computed to be 283.1 days for Single-Bond adhesive and 112.3 days for Prime and Bond NT adhesive. Storage recommendations for both adhesive systems comprise: they can be stored at room temperature, should be capped immediately after use to minimize evaporation, should not be exposed to high temperatures or intense light; they are designed to be used at room temperature of approximately 21-24°C (or 70-75°F), and the shelf life (vial delivery) is 36 months at room temperature. However, these results are not comparable to the findings of the present study because of different methodologies.

Different solvents have been used in dentin bonding systems, such as acetone, water, and ethanol. Acetone and organic solvents miscible in water allow chemical removal of water by diffusion in demineralised dentin and facilitate the infiltration of resin monomers (15). When these organic solvents evaporate after the adhesive application on dentin surface, monomers are absorbed by collagen fibbers in demineralised dentine, and monomer concentration increases (16). Solvent loss may not permit a high enough concentration of monomer to form a uniform film on dentin surface and may change the shear bond strength of acetone-based adhesive systems to dentin. This might explain the variations in bond strength values reported in the literature (17). In experimental dentin bonding agents with increasing acetone content, microtensile bond strength varied from 38 MPa (67% acetone) to 64 MPa (37% acetone), showing that variation of solvent content affects adhesion to dentin (18).

Determination of water content in Single Bond

The results of water content in Single Bond by Karl Fischer Titration were summarized in Table 3. The water content was determined for each temperature and at baseline and final incubation period. The amount of total water present in Single-Bond adhesive corresponded to 5.90% of total solvent. Water percentage was reduced as temperature increased, which indicates that water loss occurred next to ethanol. Organic solvents miscible in water are considered azeotropic mixtures. When warming up an azeotropic mixture the steam has the same composition than the liquid, therefore the obtained distilled compound has the same composition of the original liquid, and the components are not separated in the process. This means that ethanol evaporates next to water (19). When ethanol/water-based adhesive systems are used, failure to remove water could result in dilution of water-soluble resin components, reducing the degree of conversion of bonding resins and thus compromising hybrid layer formation (20).

Table 3. Water content of Single Bond in different temperatures after 15 days

Temperature	% water
20°C	5.90±0.08
25°C	5.49±0.16
30°C	5.09±0.09
40°C	4.41±0.07
50°C	1.76±0.38

Determination of total solvent in Single Bond and Prime and Bond NT

The weight constant of Single Bond specimens incubated at 80°C after 15 days was 6.16±0.04 grams, which corresponds to the adhesive solute mass. Once the water percentage and total percentage of solvent (45.04±1.19%) are known, it is possible to determine the content of alcohol (39.14±1.19%). For Prime and Bond NT adhesive the weight constant was 4.79±0.12 grams and the content of acetone was 43.08±1.15%.

Prime and Bond NT and Single Bond lowest pH values were 2.1 and 4.6, respectively, which is possibly related to the presence of acidic monomers in their compositions. However, no relation between solvent acidity and its speed of evaporation was found.

Conclusions

At room temperature, as determined by this stability study, it was predicted that the tested acetone-based adhesive has the greatest solvent loss. The adhesives with volatile solvents should be stored preferably under refrigeration because they would present maximum chemical stability.

References

1. Nakabayashi N, Pashley DH. Hybridization of dental hard tissues. Characterization of the hybrid layer. Tokio: Quintessence publishing Co. 2000. p. 5-16.
2. Tay FR, Gwinnett JA, Wei SH. Micromorphological spectrum from overdrying to overwetting acid-conditioned dentin in water-free acetone-based, single-bottle primer/adhesives. Dent Mater 1996;12:236-44.
3. Vargas MA, Cobb DS, Denehy GE. Interfacial micromorphology and shear bond strength of single-bottle primer/adhesives. Dent Mater 1997;13:316-24.
4. Eick JD, Gwinnett AJ, Pashley DH, Robinson SJ. Current concepts on adhesion to dentin. Crit Rev Oral Biol Med 1997;8:306-35.
5. Swift EJ Jr. Bonding systems for restorative materials – a comprehensive review. Pediatr Dent 1998;20:80-4.

6. Van Meerbeek B, Dhem A, Goret-Nicaise M, Braem M, Lambrechts P, VanHerle G. Comparative SEM and TEM examination of the ultrastructure of the resin-dentin interdiffusion zone. J Dent Res 1993;72:495-501.
7. Perdigão J, Van Meerbeek B, Lopes MM, Ambrose W. The effect or re-wetting agent on dentin bonding. Dent Mater 1999;15: 282-95.
8. Maciel KT, Carvalho RM, Ringle RD, Preston CD, Russell CM, Pashley DH.The effects of acetone, ethanol, hema and air on the stiffness of human decalcified dentin matrix. J Dent Res 1996;75:1851-8.
9. Bouillaguet S, Gysi P, Wataha JC, Ciucchi B, Cattani M, Godin C et al. Bond strength of composite to dentin using conventional, one-step, and self-etching adhesive systems. J. Dent. 2001;29: 55-61.
10. Titration KF. Monograph No. 8.026.5003: Water determination. Herisau: Metrohm; [2007].
11. Hashimoto M, Ohno H, Kaga M, Sano H, Tay FR, Oguchi H et al. Over-etching effects on micro-tensile bond strength and failure patterns for two dentin bonding systems. J Dent 2002;30:99-105.
12. Hashimoto M, Ohno H, Kaga MF, Sano H, Endo K, Oguchi H. Fractured surface characterization: wet versus dry bonding. Dent Mater 2002;18:95-102.
13. Kirkwood TB. Design and analysis of accelerated degradation test for the stability of biological standard III. Principles of design. J Biol Stand 1984;12:215-24.
14. Kirkwood TB. Predicting the stability of biological standard and products. Biometrics 1970;33:736-42.
15. Perdigão J, Ramos JC, Lambrechts P. In vitro interfacial relationship between human dentin and one-bottle dental adhesives. Dent Mater 1997;13:218-27.
16. Nakajima M, Kanemura N, Pereira PN, Tagami J, Pashley DH. Comparative microtensile bond strength and SEM analysis of bonding to wet and dry dentin. Am J Dent 2000;13:324-8.
17. Lopes GC, Cardoso PC, Vieira LC, Baratieri LN, Rampinelli K, Costa G. Shear bond strength of acetone-based one-bottle adhesive systems. Braz Dent J 2006;17:39-43.
18. Cho BH, Dickens SH. Effects of the acetone content of single solution dentin bonding agents on the adhesive layer thickness and the microtensile bond strength. Dent Mater 2004;20: 107-15.
19. Castellan GW. Fisicoquímica: soluciones. 2. ed. Wilmington: Addison Wesley Iberoamericana; 1987. p.324-8.
20. Reis A, Loguercio AD, Azevedo CL, de Carvalho RM, da Julio Singer M, Grande RH. Moisture spectrum of demineralized dentin for adhesive systems with different solvent bases. J Adhes Dent 2003;5:183-92.