Published in final edited form as:

Dent Mater. 2010 April ; 26(4): . doi:10.1016/j.dental.2009.11.078.

Influence of different initiators on the degree of conversion of experimental adhesive blends in relation to their hydrophilicity and solvent content

Milena Cadenaro¹, Francesca Antonioli¹, Barbara Codan¹, Kelli Agee², Franklin R Tay², Elettra De Stefano Dorigo¹, David H Pashley², and Lorenzo Breschi^{1,3}

¹Unit of Dental Sciences and Biomaterials, Department of Biomedicine, University of Trieste, Italy

²Department of Oral Biology, School of Dentistry, Medical College of Georgia, Augusta, Georgia, USA

³IGM-CNR, Unit of Bologna c/o IOR, Bologna, Italy

Abstract

Objectives—The aim of this study was to compare the curing reaction of five experimental adhesive blends containing different photo-initiating systems. The hypothesis tested was that degree of conversion (DC) of resin blends is affected by resin type, solvent content and photo-initiating system.

Methods—The experimental methacrylate resin blends were ranked from hydrophobic (R2) to hydrophilic (R3 and R4) and tested as neat, or solvated with 10% or 20% ethanol, or 10% ethanol and 10% water. Three different photo-initiators were used: IS-1 = 0.25% CQ (camphorquinone) + 1% EDMAB (ethyl 4-dimethylaminobenzoate); IS-2 = 1.25% TPO (diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide); IS-3 = 0.25% CQ + 0.50% EDMAB + 0.50% TPO. DC of resin blends was measured with a differential scanning calorimeter. Data were analyzed with a three-way ANOVA.

Results—Neat resin type influenced DC, as R4 showed the highest values compared to R2 and R3 ($p < 0.05$). Solvent had a significant effect on DC ($p < 0.05$): dilution of resin blends with 10% or 20% ethanol or 10% ethanol + 10% water increased the DC of all resins, except for R4. Initiators influenced the polymerization since neat resins and mixtures solvated with 10 or 20% ethanol showed their highest DC values when polymerized with IS-1 or IS-3 ($p > 0.05$), while IS-2 or IS-3 increased the DC values of resins diluted with 10% ethanol and 10% water ($p < 0.05$).

Conclusions—Water-compatible photo-initiators such as TPO should be included in the hydrophilic solvated adhesive formulation to ensure an appropriate DC of the adhesive layer.

Keywords

dentin-bonding agents; degree of conversion; initiators; hydrophilicity; solvent

INTRODUCTION

All contemporary dental adhesives contain hydrophilic methacrylates and hydrophobic dimethacrylates to bond to wet vital dentin and to restorative materials, respectively. Solvents and polymerization initiator systems are added to complete the adhesive

formulations with the attempt to increase wettability and create a single-phase solution. Three-step etch-and-rinse and two-step self-etch primer adhesives cover their primers with a separate layer of unsolvated hydrophobic resin. In contrast, in simplified adhesives (two-step etch-and-rinse and one-step self-etch formulations respectively), the manufacturers have combined the hydrophilic primers with the hydrophobic dimethacrylates and solvent to increase their hydrophilicity [1]. The lack of an unsolvated, relatively hydrophobic layer in simplified adhesive interfaces allows water to flow from the underlying dentin substrate to the top of the adhesive layer [2–5], thus confirming that simplified adhesives behave as permeable membranes after polymerization [6].

Besides the hydrophilicity of the resin blends, the permeability of the adhesive interface has also been correlated to solvent content and degree of cure (DC) [7,8]. That is, higher solvent percentages blended within simplified adhesives produced lower DC and higher permeability [9,10]. During the curing reaction, hydrophilic and hydrophobic domains containing polymer chains should sufficiently cross-link to make the resin strong enough to serve as bonding agent. Previous studies revealed that the polymerization reaction of these amphiphilic resin blends is frequently incomplete due to several factors affecting the DC: monomer structure and functionality [11], comonomer composition [12], adhesive hydrophilicity [7], solvent type and concentration [7,8,13] and presence of water [14] are some of the most investigated factors affecting polymerization.

Nano-phase separation phenomena have been frequently revealed, mainly within simplified adhesives, due to the simultaneous presence of hydrophilic and hydrophobic domains [15]. Ye *et al.* [16,17] using tapping mode atomic force microscopy imaging, confirmed a nano-scale phase separation for all cross-linked polymethacrylates related to BisGMA/HEMA and water concentration. The most hydrophilic domains (poly(HEMA)-rich segments linked to water) separate from poly(BisGMA)-rich hydrophobic areas creating heterogeneous resin blends. As camphorquinone (CQ), the most common photo-initiator, is hydrophobic, hydrophilic monomers may suboptimally polymerize due to inappropriate polymerization initiation, and this may explain why simplified adhesives exhibited lower degree of cure if compared to unsimplified counterparts.

To improve the DC of simplified adhesives, the use of additional hydrophilic photo-initiators, in addition to standard CQ activation, has been proposed [18,19]. Indeed, the addition of a water-compatible component to photo-initiators reduced the detrimental effect of phase separation and improved the performances of the adhesives promoting polymerization of both hydrophilic and hydrophobic domains [17].

However little is known on the use of CQ-alternative co-initiators (such as TPO: ethyl 4-dimethylaminobenzoate and diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide) on the polymerization of hydrophilic dental adhesives. Thus the aim of the present study was to investigate polymerization of three experimental adhesive blends with respect to their hydrophilicity, solvent and water content. The hypotheses tested were that the DC of the adhesive blend is insensitive to (1) resin hydrophilicity, (2) solvent/water content and (3) incorporation of a CQ-alternative hydrophilic photo-initiator.

MATERIALS AND METHODS

Three experimental resin blends with increasing hydrophilicity were investigated. R2 (70% BisGMA, 28.75% TEGDMA) is similar to a nonsolvated hydrophobic resins used in the formulation of a two-step self-etch adhesive; R3 (70% BisGMA, 28.75% HEMA) is representative of a two-step etch-and-rinse adhesive, while R4 (40% BisGMA, 30% TCDM, 28.75% TEGDMA) is the most hydrophilic blend tested, and is similar to the formulation of

one-step self-etch adhesives. All compositions expressed in terms of total weight percentage are listed in Table 1.

Absolute ethanol and deionized water in different mass percentages (A: 0%, B: 10% ethanol, C: 20% ethanol, D: 10% ethanol and 10% water) were added to the resin blends (Table 1).

Three different photo-initiating systems were prepared using CQ, ethyl 4-dimethylaminobenzoate (EDMAB) and TPO (all reagents purchased from Sigma-Aldrich, St. Louis, MO, US): IS-1 = 0.25% CQ + 1% EDMAB; IS-2 = 1.25% TPO; IS-3 = 0.25% CQ + 0.50% EDMAB + 0.50% TPO (Table 1). Stock mixtures were prepared by incorporating all components in dark bottles and by stirring them for 2 min by means of a vortex mixer (Vortex Classic, Velp Scientifica, Milano, Italy).

A Differential Scanning Calorimeter (DSC, Q10 TA Instruments, New Castle, DE, USA) was used to measure the extent of polymerization of resin blends as a function of resin hydrophilicity, solvent, and photo-initiator. The resin/solvent/initiator mixtures (average mass = 3.0 mg) were placed in pans with a transparent cover to avoid solvent evaporation and polymerized in the DSC chamber. Curing was performed at a constant temperature of 35°C in a nitrogen-purged environment using a quartz-halogen curing unit (Elipar 2500, 3M ESPE, St. Paul, MN, USA; irradiance was previously checked at 600 mW/cm²). The curing procedure was performed up to 120 s. DSC analysis was conducted in accordance with previous studies [7,9,10]. In brief, two aluminum pans were placed in the sample holder of the calorimeter chamber: one with the tested specimens and the other empty as a reference. The DSC chamber was covered by an aluminum cover with a round hole and a thin quartz disk to allow light to pass through and permit curing of the specimen inside the calorimeter at a minimum distance of 5 mm. A custom made support held the lamp during polymerization to fully irradiate the specimen-containing pan. The irradiance of the curing unit through the quartz disk at a distance of 5 mm (i.e. as to simulate the actual irradiance on the specimen surface) was 495 mW/cm² (measured using a power meter PM100, Thorlabs, Karlsfeld, Germany). Calorimetric analysis consisted of two consecutive light exposures: the first light exposure to the specimens to produce complete polymerization, and the second exposure to the same fully cured specimens to evaluate irradiation heat flow from the light-curing unit. The heat of reaction obtained from the first scan represented the sum of the exothermic effect due to monomer conversion plus the heat flow from the curing unit, while the heat flow measured in the second scan was attributed to the irradiation heat output of the lamp. The heat of resin polymerization was calculated by subtracting the heat value of the second exotherm from the value obtained after the first light exposure. Extent of polymerization expressed as percentage and normalized by the sample weight was then calculated from exotherms at the clinically relevant irradiation time of 20 s using the equation:

$$E_p = \frac{\int_0^{t_x} W_g(t) dt}{\int_0^{t_{tot}} W_g(t) dt} \cdot 100$$

where W_g = heat flow normalized by monomer sample weight, t = time, t_{tot} = total time and $x = 20$ s [7,9,10]. The degree of conversion was determined by detecting changes in heat release during the polymerization procedure and conversion was calculated from the theoretic heat release per mole reacted carbon double bond (56.92 kJ/mol) [20].

Data were analyzed with a three-way ANOVA to investigate the effect of resin hydrophilicity, solvent (type and concentration) and photo-initiator. Differences between groups were calculated using Tukey's post hoc test. Statistical significance was preset at $p = 0.05$.

RESULTS

Mean values and standard deviations (SD) of the DC of the 3 neat resins and their respective resin/ethanol/water mixtures, with different photo-initiating systems are reported in Table 2. Representative DSC curves of the resin mixtures solvated with 20% ethanol or 10% ethanol and 10% water tested with different initiators systems are reported in Fig. 1–2.

Resin type and its hydrophilicity influenced DC, as R4 showed the highest values compared to R2 and R3 ($p < 0.05$).

Solvent had a significant effect on DC ($p < 0.05$). Dilution of resin neat blends with a 10% or 20% ethanol or 10% ethanol + 10% water increased the DC irrespective from resin type, with the exception for R4, as a significant reduction was observed when 10% ethanol and 10% water were added to R4 with CQ and EDMAB only (IS-1; $p < 0.05$).

A significant interaction was observed between solvent type and photo-initiators ($p < 0.05$). Neat resins and mixtures solvated with 10 or 20% ethanol showed their highest DC values when polymerized with CQ (IS-1; $p < 0.05$) or CQ+TPO (IS-3; $p < 0.05$). On the other hand TPO (IS-2) or CQ+TPO (IS-3) increased the DC values of all resins diluted with 10% ethanol and 10% water ($p < 0.05$).

In Fig. 3, the degree of conversion (DC) is plotted against the Hoy's solubility parameter for hydrogen bonding (δ_h). The curve shows that there is a high correlation ($R^2 = 0.99$) between these two variables. The curve is in four segments beginning with the neat resin 2–4 at the far left show DC values of about 60%. There are six data points: three for resins 2–4 polymerized by CQ/EDMAB (IS-1) and three for resins 2–4 polymerized by CQ/EDMAB/TPO (IS-3). Moving up the curve, the next cluster of data points are the same resins solvated with 10% ethanol. Further up the curve, the same resins were solvated with 20% ethanol. Finally, at the far right side of the curve are the same resins solvated with 10% ethanol plus 10% water. Note that this final solvent mixture had no effect on the DC of resin 2–4 polymerized by IS-3, but it significantly ($p < 0.05$) lowered the DC of resins 3 and 4 polymerized by IS-1 (CQ/EDMAB without TPO).

DISCUSSION

The results of this study demonstrated that DC differed between the tested adhesive blends, in relation to resin type (and its hydrophilicity), solvent content and photo-initiator used. Thus the tested hypotheses were rejected.

DC of dental adhesives is an important parameter as low mechanical properties [21] and monomer elution [22,23] are related with low percentage of monomer to polymer conversion within resin-based materials. Low degrees of conversion have also been associated with increased permeability [9,10], phase separation [18], and droplets formation within the adhesive layer due to the higher susceptibility to water sorption of suboptimally cured adhesives [18,24–26]. Reduced degree of conversion accounts even for the possible continuous etching of dentin due to suboptimally polymerized acidic monomers in self-etch adhesives. [27,28]. In the present study, R4, (representative of a one-step self-etch adhesive) contains sufficient acidic monomer to give it a pH of 5.0 in the presence of water [7], thus if not properly polymerized, it may demineralize the dentin structure within the hybrid layer.

The results of this study revealed that when the neat resin blends were tested, the hydrophobic resin blend (R2) showed slightly lower DC than the more hydrophilic blends (R3 and R4), regardless of the type of photo-initiators (Table 2) used ($p < 0.05$). The different degree of conversion of experimental resins should be probably ascribed to the different chemical structures of the dimethacrylate monomers in the resin mixtures. Reductions in crosslink density obtained by use of higher molecular weight monomers or monomers with lower degrees of functionality enhance overall mobility and conversion. R2 contains large amounts of Bis-GMA which is a poorly flexible monomer characterized by two pendant hydroxyl groups and TEGDMA [21], resulting in a quite viscous resin blend. Since high viscosity indicates the presence of intermolecular interactions, viscous resins show reduced monomers mobility during polymerization [7], finally counteracting the curing process. R3 contains Bis-GMA and HEMA that compared to TEGDMA is a much smaller and less viscous molecule. The DC of R3 was probably enhanced (compared to R2, $p < 0.05$) due to the HEMA-induced effect of lower viscosity and higher mobility of the polymer chains. Although R4 also contains TEGDMA, its formulation is based on more hydrophilic and acidic monomers and a lower Bis-GMA content. If no solvent is present, the low viscosity of the resin blend may justify its higher DC compared to R2 ($p < 0.05$) [7].

There was a significant ($p < 0.05$) positive correlation between DC and the hydrophilicity of the tested resin blends (Fig. 3). As solvents were added to the neat resins, the blends became more hydrophilic (i.e. had higher χ_h values).

Besides hydrophilicity, the curing reaction was clearly affected by solvents. Our results showed that addition of 10% and especially 20% ethanol significantly increased the DC (irrespective of resin type, $p < 0.05$). These data are consistent with previous study [7,8,13,29] confirming that the addition of small amounts of ethanol enhances the degree of conversion of the adhesive mixtures through the increase of polymer chain mobility and radical diffusion rate.

On the other hand, the addition of 10% ethanol and 10% water significantly decreased the DC of resin mixtures when using CQ (IS-1) as photo-initiator, particularly for R3 and R4 (Figs. 2 and 3). This confirms that water interferes with the polymerization process of adhesive mixtures [14,30,31], influencing the component reactivity and diluting the adhesive monomers [30]. Additionally, since CQ is hydrophobic, its reactivity with hydrophilic domains can be reduced. However, when those same 10% ethanol/10% H₂O solvated resin 2–4 were polymerized using CQ/EDMAB/TPO, there was no reduction in DC. It is likely that TPO dissolved in the water enough to counteract the exclusion of CQ from that aqueous domain (Fig. 3).

It has been shown that even though CQ and tertiary amines coinitiators (such as ethyl 4-dimethylaminobenzoate, EDMAB) are the most common photo-initiating systems in dental resin restorative materials [32], they present some undesirable adverse effects such as the color of the composite restoration (that can be negatively affected by the yellow-colored CQ) [33], and the reduced reactivity of the amine co-initiator that may be neutralized by the low pH of self-etch adhesives [34,35]. Recently, photo-initiating systems in which no co-initiators are needed, such as the Norrish Type I photo-initiators [36], were proposed for dental applications. Within this photo-initiators' group only acylphosphine oxides, such as Lucirin TPO, has been used in commercially available products [36]. In a previous study comparing experimental adhesives containing TPO-based photo-initiators with their commercial counterparts containing CQ, comparable DC values were obtained [19], while in another report TPO showed a higher efficiency compared to CQ, phenylpropanedione (PPD), and bisacylphosphine oxide (Irgacure 819), when a methyl methacrylate monomer was polymerized with a halogen light curing unit [37]. In the present study TPO alone (IS-2)

only increased the DC of resin mixtures solvated with 10% ethanol plus 10% water. When TPO was combined with CQ (IS-3) it produced DC values comparable to CQ alone (IS-1) for neat resins and ethanol-solvated mixtures. When Hoy's solubility parameter for total cohesive strength (γ_t) was calculated, TPO was the most hydrophilic of the EDMAB, CQ, TPO series ($\gamma_t = 18.8, 20.0$ and 23.40 (MPa)^{1/2}, respectively). That is, it would be the most water soluble.

While the effective wavelength range of CQ is between 400 and 500 nm [37] thus compatible with the emission spectra of most of the halogen and LED curing units, a major drawback of acylphosphine oxides is that their absorption peak is at 390 nm, making it unsuitable with several LED polymerization light units (emitting light in the wavelength range of 450 to 500 nm)[38]. For this reason, in this study a halogen light-curing unit was chosen to adequately activate both CQ and TPO. Molar absorptivity of the initiators in relation to the curing unit used could have influenced their efficiency. This aspect should be investigated in further studies.

Within the limitations of this study, the results suggest that the photo-initiating system should be selected according to adhesive system composition, considering the presence of residual water and/or solvents. Water-compatible photo-initiators should be included within the solvated hydrophilic adhesive formulations to ensure an appropriate DC of the adhesive layer and reduce aging phenomena.

Acknowledgments

This work was supported, in part, by R01 DE014911-06 from the National Institute of Dental and Craniofacial Research, P.I. (DHP).

References

1. Tay FR, Pashley DH. Have dentin adhesives become too hydrophilic? J Can Dent Assoc. 2003; 69:724–731.
2. Sano H, Yoshikawa T, Pereira PN, Kanemura N, Morigami M, Tagami J, Pashley DH. Long-term durability of dentin bonds made with a self-etching primer, in vivo. J Dent Res. 1999; 78:906–911. [PubMed: 10326735]
3. Burrow MF, Inokoshi S, Tagami J. Water sorption of several bonding resins. Am J Dent. 1999; 12:295–298. [PubMed: 10850250]
4. Takahashi A, Inoue S, Kawamoto C, Ominato R, Tanaka T, Sato Y, Pereira PN, Sano H. In vivo long-term durability of the bond to dentin using two adhesive systems. J Adhes Dent. 2002; 4:151–159. [PubMed: 12236644]
5. De Munck J, Van Meerbeek B, Yoshida Y, Inoue S, Vargas M, Suzuki K, Lambrechts P, Vanherle G. Four-year water degradation of total-etch adhesives bonded to dentin. J Dent Res. 2003; 82:136–140. [PubMed: 12562888]
6. Tay FR, Pashley DH, Suh BI, Carvalho RM, Itthagarun A. Single-step adhesives are permeable membranes. J Dent. 2002; 30:371–382. [PubMed: 12554121]
7. Cadenaro M, Breschi L, Antonioli F, Navarra CO, Mazzoni A, Tay FR, Di Lenarda R, Pashley DH. Degree of conversion of resin blends in relation to ethanol content and hydrophilicity. Dent Mater. 2008; 24:1194–1200. [PubMed: 18342363]
8. Cadenaro M, Breschi L, Rueggeberg Fa, Suchko M, Grodin E, Agee K, Di Lenarda R, Tay FR, Pashley DH. Effects of residual ethanol on the rate and degree of conversion of five experimental resins. Dent Mater. 2009; 25:621–628. [PubMed: 19111335]
9. Cadenaro M, Antonioli F, Sauro S, Tay FR, Di Lenarda R, Prati C, Biasotto M, Contardo L, Breschi L. Degree of conversion and permeability of dental adhesives. Eur J Oral Sci. 2005; 113:525–30. [PubMed: 16324144]

10. Breschi L, Cadenaro M, Antonioli F, Sauro S, Biasotto M, Prati C, Tay FR, Di Lenarda R. Polymerization kinetics of dental adhesives cured with LED: Correlation between extent of conversion and permeability. *Dent Mater.* 2007; 23:1066–1072. [PubMed: 17109951]
11. Anseth KS, Kline LM, Walker TA, Anderson KJ, Bowman CN. Reaction kinetics and volume relaxation during polymerizations of multiethylene glycol dimethacrylates. *Macromolecules.* 1995; 28:2491–2499.
12. Shobha HK, Sankarapandian M, Sun Y, Kalachandra S, McGrath JE, Taylor DF. Effect of dilution on the kinetics of cross-linking thermal polymerization of dental composite matrix resins. *J Mater Sci Mater Med.* 1997; 8:583–586. [PubMed: 15348825]
13. Malacarne-Zanon J, Pashley DH, Agee KA, Foulger S, Corrêa-Alves M, Breschi L, Cadenaro M, Garcia FP, Carrilho MR. Effects of ethanol addition on the water sorption/solubility and percent of comonomers conversion in model dental adhesives. *Dent Mater.* in press.
14. Paul SJ, Leach M, Rueggeberg FA, Pashley DH. Effect of water content on the physical properties of model dentine primer and bonding resins. *J Dent.* 1999; 27:209–214. [PubMed: 10079627]
15. Tay FR, Pashley DH, Yoshiyama M. Two modes of nanoleakage expression in single-step adhesives. *J Dent Res.* 2002; 81:472–476. [PubMed: 12161459]
16. Ye Q, Spencer P, Wang Y. Nanoscale Patterning in Crosslinked Methacrylate Copolymer Networks: An Atomic Force Microscopy Study. *J Appl Polym Sci Symp.* 2007; 106:3843–3851. [PubMed: 19081742]
17. Ye Q, Park Jg, Topp E, Wang Y, Misra A, Spencer P. In vitro performance of nano-heterogeneous dentin adhesive. *J Dent Res.* 2008; 87:829–833. [PubMed: 18719208]
18. Wang Y, Spencer P, Yao X, Ye Q. Effect of coinitiator and water on the photoreactivity and photopolymerization of HEMA/camphoroquinone-based reactant mixtures. *J Biomed Mater Res.* 2006; 78A:721–728.
19. Ilie N, Hickel R. Can CQ be completely replaced by alternative initiators in dental adhesives? *Dent Mater J.* 2008; 27:221–228. [PubMed: 18540396]
20. Odian, G. Principles of polymerization. New York: Wiley; 1981.
21. Ferracane JL, Greener EH. The effect of resin formulation on the degree of conversion and mechanical properties of dental restorative resins. *J Biomed Mater Res.* 1986; 20(1):121–131. [PubMed: 3949822]
22. Ferracane JL. Elution of leachable components from composites. *J Oral Rehabil.* 1994; 21(4):441–452. [PubMed: 7965355]
23. Munksgaard EC, Peutzfeldt A, Asmussen E. Elution of TEGDMA and BisGMA from a resin and a resin composite cured with halogen or plasma light. *Eur J Oral Sci.* 2000; 108(4):341–345. [PubMed: 10946770]
24. Van Landuyt KL, Cardoso MV, De Munck J, Peumans M, Mine A, Lambrechts P, Van Meerbeek B. Optimization of the concentration of photo-initiator in a one-step self-etch adhesive. *Dent Mater.* 2009 Epub ahead of print.
25. Tay FR, Gwinnett AJ, Wei SHY. The overwet phenomenon: A transmission electron microscopic study of surface moisture in the acid-conditioned, resin-dentin interface. *Am J Dent.* 1996; 9:161–166. [PubMed: 9002792]
26. Tay FR, Gwinnett AJ, Pang KM, Wei SHY. An optical, micromorphological study of surface moisture in the total etched resin-dentin interface. *Am J Dent.* 1996; 9:43–48. [PubMed: 9002816]
27. Wang Y, Spencer P. Continuing etching of an all-in-one adhesive in wet dentin tubules. *J Dent Res.* 2005; 84:350–354. [PubMed: 15790742]
28. Wang Y, Spencer P. Physicochemical interactions at the interfaces between self-etch adhesive systems and dentin. *J Dent.* 2004; 32:567–579. [PubMed: 15386864]
29. Ye Q, Wang Y, Williams K, Spencer P. Characterization of photopolymerization of dental adhesives as a function of light source and irradiance. *J Biomed Mater Res Part B: Appl Biomaterials.* 2007; 80B:440–446.
30. Jacobsen T, Soderholm K-J. Some effects of water on dentin bonding. *Dent Mater.* 1995; 11:132–136. [PubMed: 8621034]
31. Spencer P, Wang Y. Adhesive phase separation at the dentin interface under wet bonding conditions. *J Biomed Mater Res.* 2002; 62:447–456. [PubMed: 12209931]

32. Jakubiak J, Allonas X, Fouassier JP, Sionkowska A, Andrzejewska E, Linden LÅ, Rabek JF. Camphorquinone-amines photoinitiating systems for the initiation of free radical polymerization. *Polymer*. 2003; 44:5219–5226.
33. Janda R, Roulet JF, Kaminsky M, Steffin G, Latta M. Color stability of resin matrix restorative materials as a function of the method of light activation. *Eur J Oral Sci*. 2004; 112:280–285. [PubMed: 15154928]
34. Cheong C, King NM, Pashley DH, Ferrari M, Toledano M, Tay FR. Incompatibility of self-etch adhesives with chemical/dual-cured composites: two-step vs one-step systems. *Oper Dent*. 2003; 28:747–755. [PubMed: 14653290]
35. Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interaction between one-bottle light-cured adhesives and chemical-cured composites. *Dent Mater*. 2001; 17:542–556. [PubMed: 11567693]
36. Moszner N, Salz U, Zimmermann J. Chemical aspects of self-etching enamel–dentin adhesives: A systematic review. *Dent Mater*. 2005; 21:895–910. [PubMed: 16038969]
37. Neumann MG, Miranda WG Jr, Schmitt CC, Rueggeberg FA, Correa IC. Molar extinction coefficients and the photon absorption efficiency of dental photoinitiators and light curing units. *J Dent*. 2005; 33:525–532. [PubMed: 15935273]
38. BASF Corporation. Lucirin TPO, Technical Information. 2001. <http://www.basf.com/rawmaterials/pdfs/LUC-TPO.pdf>

Figure 1

Figure 2

Figures 1–2.

Representative DSC curves of the resin mixtures solvated with 20% ethanol or 10% ethanol and 10% water tested with different initiators systems: R2 was the less affected by the presence of water compared to R3 and R4 that showed a smaller and broader peak related to the slower speed of reaction if IS-1 was used. TPO (IS-2 and IS-3) was needed to speed up the polymerization reaction.

Figure 3.

The degree of conversion of neat vs. solvated resins 2–4 activated by CQ/EDMAB alone (IS-1), TPO alone (IS-2) or CQ/EDMAB/TPO (IS-3) are plotted against the Hoy's solubility parameter for hydrogen bonding cohesive forces, δ_h in (MPa)^{1/2}. As the neat resins were solvated by 10 or 20% ethanol or 10% ethanol/10% water, the hydrophilicities of all of the resins increased. However, the DC of resins 3 and 4 polymerized with IS-1 fell when solvated with 10% ethanol/10% water. This was not the case when the resins were polymerized with IS-2 or IS-3. The R^2 and p values were calculated without those two data points.

Table 1
Composition (wt%) of experimental resins 2–4 and Hoy's solubility parameters () for the comonomers.

Resin #	Neat Resin Composition	IS 1				IS 2				IS 3			
		d	p	h	t	d	p	h	t	d	p	h	t
R2	Neat resin	15.86	12.38	6.53	21.15	15.89	12.42	6.47	21.19	15.87	12.40	6.51	21.17
	10%ETH	15.41	12.21	8.40	21.38	15.44	12.25	8.35	21.4	15.42	12.23	8.38	21.39
	20%ETH	15.00	12.06	10.12	21.74	15.02	12.09	10.07	21.75	15.00	12.07	10.10	21.75
	10%ETH+10%H ₂ O	15.02	13.33	12.03	23.41	15.04	13.36	11.99	23.42	15.02	13.35	12.02	23.42
R3	Neat resin	15.58	13.02	8.68	22.08	15.62	13.07	8.62	22.11	15.59	13.04	8.67	22.10
	10%ETH	15.17	12.76	10.24	22.32	15.20	12.81	10.19	22.34	15.18	12.78	10.24	22.33
	20%ETH	14.79	12.53	11.68	22.64	14.82	12.57	11.64	22.65	14.8	12.54	11.68	22.64
	10%ETH+10%H ₂ O	14.81	13.81	13.64	24.41	14.84	13.85	13.59	24.43	14.81	13.83	13.63	24.42
R4	Neat resin	16.41	12.81	6.99	21.96	16.45	12.86	6.92	21.99	16.42	12.83	6.97	21.98
	10%ETH	15.87	12.58	8.84	22.10	15.91	12.62	8.78	22.12	15.88	12.59	8.82	22.10
	20%ETH	15.38	12.36	10.52	22.36	15.41	12.40	10.47	22.38	15.39	12.38	10.51	22.37
	10%ETH+10%H ₂ O	15.41	13.67	12.49	24.09	15.44	13.71	12.44	24.11	15.42	13.69	12.47	24.10

Abbreviations: BisGMA = 2,2-bis[4-(2-hydroxy-3-methacryloylpropoxy)-1-phenyl]propane; TEGDMA = triethyleneglycol dimethacrylate; HEMA = 2-hydroxyethyl methacrylate; TCDM = di(hydroxyethylmethacrylate)ester of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexane-1, 2 -dicarboxylic acid. All solubility parameters were calculated using commercially available software (Computer Chemistry Consultancy <www.compchemconsult.com>. d = Hoy's solubility parameter for dispersive forces; p = Hoy's solubility parameter for polar forces; h = Hoy's solubility parameters for hydrogen bonding forces; t = Hoy's solubility parameter for total cohesive forces, equivalent to Hildebrand's solubility parameter (). $t = [(d)^2 + (p)^2 + (h)^2]^{1/2}$. All Hoy's values given in (J/cm³)^{1/2}.

Table 2

Percent monomer degree of conversion (DC%) values for three experimental resins and their respective resin/ethanol/water mixtures (wt%), with the different initiator systems at 20 s.

		IS 1	IS 2	IS 3
R2	Neat resin	62.6 (0.4) ^{bc}	59.1 (0.9) ^{ab}	62.3 (0.4) ^{bc}
	10%ETH	73.7 (1.8) ^{gh}	72.1 (2.3) ^{fg}	73.6 (2.2) ^{gh}
	20%ETH	77.8 (0.5) ^{ijk}	76.4 (1.1) ^{hi}	76.7 (0.9) ^{hij}
	10%ETH+10%H ₂ O	78.0 (2.5) ^{ijl}	81.7 (2.7) ^{mn}	80.7 (1.2) ^{klmn}
R3	Neat resin	66.3 (1.1) ^{de}	63.7 (1.2) ^{cd}	66.4 (0.7) ^{de}
	10%ETH	75.2 (2.1) ^{ghi}	75.0 (1.4) ^{ghi}	78.4 (1.4) ^{ijklm}
	20%ETH	77.9 (1.7) ^{ijkl}	72.3 (0.6) ^g	78.5 (1.9) ^{ijklm}
	10%ETH+10%H ₂ O	67.7 (2.2) ^e	81.8 (0.8) ^{mn}	81.7 (1.1) ^{mn}
R4	Neat resin	67.2 (0.5) ^{de}	66.5 (0.6) ^d	68.5 (1.1) ^{ef}
	10%ETH	75.7 (2.2) ^{ghi}	73.9 (1.3) ^{gh}	81.7 (1.4) ^{mn}
	20%ETH	77.1 (1.2) ^{hijk}	77.6 (1.0) ^{ijk}	81.4 (0.7) ^{klmn}
	10%ETH+10%H ₂ O	56.4 (1.4) ^a	83.1 (1.1) ⁿ	80.1 (1.2) ^{ijklmn}

The DC% values are expressed as mean values $\pm$ standard deviations. Means followed by the same superscript letter indicate no statistical difference ($p < .05$). IS-1 = 0.25% CQ + 1% EDMAB. IS-2 = 1.25% TPO. IS-3 = 0.25% CQ + 0.5% EDMAB + 0.5% TPO. Abbreviations: CQ = camphorquinone; EDMAB = ethyl-4-dimethylaminobenzoate; TBO = diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.