Photopolymerization Study and Adhesive Properties of Self-Etch Adhesives Containing Bis(acyl)phosphine Oxide Initiator

Authors and Affiliations:

Vincent Besse^a

Mathieu A. Derbanne^c

Thi-Nhàn Pham^a

Wayne D. Cook^b

Loïc Le Pluart^a

^a Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507, INC3M, FR 3038, ENSICAEN & Université de Caen, 14050 Caen, France

^b Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia.

^c Unité de Recherche en Biomateriaux Innovants et Interfaces (URB2I) – EA4462, Faculté de Chirurgie Dentaire, Université Paris Descartes, Sorbonne Paris Cité, 1 rue Maurice Arnoux, 92120 Montrouge, France.

First two authors have contributed equally to this work.

Corresponding Author:

Vincent Besse

Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507, INC3M, FR 3038, ENSICAEN & Université de Caen

14050 Caen, France

Phone: +33 6 25 067 059

vincentbesse@gmail.com

Photopolymerization Study and Adhesive Properties of Self-Etch Adhesives Containing Bis(acyl)phosphine Oxide Initiator

ABSTRACT

Objectives: This paper investigates the photo-co-polymerization behaviour of a blend of a diacrylamide (DEBAAP) with a phosphonylated acidic monomer using either bis(acyl)phosphine oxide or camphorquinone/amine as photo-initiator and studies the effect of variation of the structure of the phosphonylated acidic monomer on the shear bond strength to human dentine. **Methods:** Photopolymerization kinetics has been assessed through the use of photo-DSC with either initiating system and with and without a phosphonic acid monomer, while the shear bond strengths (SBS) of dentine bonding agents formulated with several phosphonylated acidic monomers have been evaluated by macro SBS testing on human dentin. **Results:** Photo-DSC results show that bis(acyl)phosphine oxide initiates a faster polymerization than camphorquinone/amine and that both photopolymerizations are accelerated by the phosphonic acid monomer. Comparable shear bond strengths were obtained but the best performances were obtained when BAPO was used as the initiator. **Significance:** The bis(acyl)phosphine oxide photoinitiator causes faster photopolymerization of two-step self-etching dental adhesive, and its use could yield better bonding performance.

KEYWORDS

Dental adhesives
Photopolymerization
Phosphine oxides
Camphorquinone
Self-Etching
Monomers
Phosphonic acid
Adhesion

1. INTRODUCTION

Photopolymerization is one of the most simple and efficient processes to form a polymer[1-3]. It is widely used in restorative dentistry and particularly for dental adhesives. For the latter, two-step self-etching adhesive systems (SEA) require the use of two separate components: a self-etching primer (SEP) used to condition the dental substrate, followed by the application of a hydrophobic bonding resin.[4-6] SEP are aqueous acidic solutions containing various vinyl monomers (acidic, hydrophilic and hydrophobic monomers) which can simultaneously etch and infiltrate dental tissues, then photopolymerize with the bonding resin, thus forming a bond between the dental substrate and the restorative material applied afterwards.[7-10] Various monomers containing phosphate esters, carboxylic and phosphonic acids have been described in the literature [8, 11-13] for use in dental adhesives. In our previous studies, we have focused on the synthesis and polymerization kinetics of novel phosphonic acid derivatives because they interact chemically with hydroxyapatite but are not subject to hydrolysis in acidic aqueous solutions in contrast to their phosphate equivalents, therefore improving the SEA's durability.[14-18]

Acidic monomers and comonomers must be capable of rapid radical polymerization. While the kinetics of free radical polymerization are rather complex for mono-vinyl systems in solution[19], multivinyl polymerization in bulk is even more complex. Indeed, rate constant for radical termination starts to drop dramatically from the start of the polymerization due to radical diffusion effects[20-22], called the Trommsdorff or gel effect, resulting in a rapid increase in the rate of polymerization before monomer depletion starts to become important. In addition, increase in the glass transition temperature (T_g) due to crosslinking process reduces the molecular mobility to such an extent that the material vitrifies leading to cessation of the propagation and termination reactions.[23, 24] In other cases where the T_g of the polymerizing matrix is below the curing temperature, the polymerization may cease prior to full reaction because the radicals and/or the reactive vinyl groups are buried in the surrounding polymerized matrix and are not able to reach fresh monomer.[7-9]

Lastly the photoinitiation system will have a major influence on the polymerization kinetics.

In our previous studies on polymerization kinetics and bond strength of two-step SEAs, we employed the commonly used camphorquinone/amine photo redox initiator system [25, 26] which has the major advantage of absorbing in the blue region of the visible spectrum and thus can be activated without UV lamps[27]. However, this system has some shortcomings since the camphorquinone has a yellowish effect[27-29], has demonstrated toxicity[30, 31] and has a low initiator efficiency.[32-34] Moreover, camphorquinone requires the presence of a photo-reducer (or co-initiator) such as a tertiary amine. Because of these drawbacks, other visible light photo initiators have emerged such as bis(acyl)phosphine oxides (BAPO).[35-39] These are classed as Norrish Type-I photo-initiators as they do not need any co-initiator since their homolytic α -cleavage is sufficient to produce two radical species both capable of initiating polymerization (Figure 1).[40-44] In terms of curing performances, resins formulated with BAPO photo-initiator usually reach a higher degree of conversion than the CQ-based ones.[45] In addition, it is non-toxic at the concentration required for clinical use. For instance, concentrations of up to 0.5 wt% (as used in this work) and up to 1.0 wt% are well tolerated by osteoblast-like cells and MC3T3 pre-osteoblasts respectively.[46, 47] Most papers describe a lower toxicity of BAPO compared to CQ and as a consequence a higher cell viability which is an obvious asset for a dental restoration.[48] However, BAPO has an absorption peak in the near UV region (UVA) which extends into the visible, thus requiring the use of specific violet (circa 390nm) light-emitting diodes (LED) for the generation of free radicals.[49, 50]

In a previous paper[51], we observed an enhanced rate of polymerization of acrylamide monomers photoinitiated by CQ/amine, when acrylamide phosphonic acids were present in the reaction medium. We also showed that this rate acceleration was not specific to the vinyl function of the phosphonic acid monomer, and was applicable to both linear polymerization and crosslinking reactions. In addition it was also shown that this effect was also observed when a non-polymerizable organic phosphonic acid was present in the polymerizing

medium. We therefore were able to conclude that the increase of the medium polarity brought by the presence of phosphonic acid moieties was responsible for the increased polymerization rate of acrylamide monomer.

One objective in this work was to investigate whether a rate enhancement through the use of phosphonic acid monomers is observed when a Norrish I type initiating system such as bis(acyl)phosphine oxide (BAPO) is used. Secondly the final extent of reaction or double bond conversion (DBC) is dependent on the monomer's chemical structure[52] but also possibly the photo initiation system and so this was also studied. The last objective of the work was to make a comparative study dealing with dentine adhesion strength tests using SEP made from a mixture of a dimethacrylamide (DEBAAP) with one of three phosphonic acid monomers (Monomers **A-C**) or a phosphoric acid monomer (**D**) using either BAPO or CQ/EDAB as photo initiating system (Figure 2).

2. MATERIAL AND METHODS

2.1. Materials

Camphorquinone (CQ) and ethyl-4-(dimethylamino)benzoate (EDAB) were purchased from Sigma Aldrich (Sigma Aldrich Corporation, Saint Louis, MO, USA). BAPO was obtained as a gift (Irgacure 819, BASF Schweiz AG, formerly CIBA AG, Basel, Switzerland). These initiators were used as components of the free radical initiation systems without further purification. A difunctional acrylamide, N,N-diethyl-bisacrylamidopropane (DEBAAP), and monomers **A-D** were synthesized according to procedures described in a previous article.[51] The structures of these monomers and initiators are given in Figure 2.

2.2. Photo-Differential Scanning Calorimetry

The photo-initiating system camphorquinone (0.54 mol% or 0.97 wt%), ethyl-4-(dimethylamino)benzoate (0.54 mol% or 1.07 wt%) or BAPO (0.54 mol% 2.26 wt%), were added to the DEBAAP and monomer A mixture for the photopolymerization studies. The concentration of 0.54 mol% for each component of the initiation system was used in order to be consistent with the previous work published by our team.[5, 6, 8, 51, 53]

The pH of each primer was measured at room temperature (22 °C) immediately after formulation by placing a drop of the primer on a glass slide and bringing it

into full contact with a flat contact electrode (PHC2441-8 Combined pH Electrode “Red Rod”) with a PHM210 Standard pH Meter (Radiometer Analytical, Villeurbanne, France).

Photopolymerization kinetics were monitored using a PerkinElmer DSC 7 differential scanning calorimeter (PerkinElmer Corporation, Waltham, MA, USA) calibrated with indium and zinc standards, which was modified to allow for irradiation of the sample and reference pans by use of a bifurcated fiber optic lead, thus minimizing the thermal heating effect of the photocuring source.[54] Approximately 3 mg of material was spread as a 0.2 mm thin layer over the base of the 4.5 mm diameter, aluminium DSC pan. To minimize the effect of dissolved oxygen on the polymerization kinetics, all resin samples were equilibrated in the apparatus for at least 5 min under a $20 \text{ cm}^3 \cdot \text{min}^{-1}$ flow of N_2 at 50°C before commencing the experiment. All photo polymerizations were performed at 50°C , using a Rofin Polilight PL400 source (Rofin Australia Pty Ltd., Dingly Victoria, Australia) with light intensities of $40 \text{ mW} \cdot \text{cm}^{-2}$ near 470 nm for CQ and $40 \text{ mW} \cdot \text{cm}^{-2}$ near 370 nm for BAPO, as measured with an Ocean Optics USB2000 fiber optic spectroradiometer (Ocean Optics Inc. Dunedin, FL, USA). An irradiation time of 600 s was used in the DSC studies for both photoinitiators. The heat flow was monitored as a function of time with the DSC under isothermal conditions. All DSC experiments were performed in duplicate with good agreement. Double-bond conversion (*DBC*) was calculated as the quotient of the overall enthalpy evolved [$\Delta H_p \text{ (J} \cdot \text{g}^{-1})$] and the theoretical enthalpy obtained for 100% conversion of the mixtures [$\Delta H_{0p} \text{ (J} \cdot \text{g}^{-1})$] (Equation 1).

$$DBC = \frac{\Delta H_p}{\Delta H_{0p}} \text{ (Equation 1)}$$

ΔH_{0p} (in $\text{J} \cdot \text{g}^{-1}$) was calculated according to the following formula (Equation 2):

$$\Delta H_{0p} = \frac{x_a \cdot \Delta H_{0a} + x_b \cdot \Delta H_{0b}}{x_a \cdot M_a + x_b \cdot M_b} \text{ (Equation 2)}$$

where x_a and x_b are the molar percentages of Monomers *a* and *b* in the mixture respectively, while M_a and M_b are their molecular weights. ΔH_{0a} and ΔH_{0b} are the

theoretical enthalpies (in J.mol⁻¹) of reaction which are 120.6 kJ.mol⁻¹ for DEBAAP[56], 60.3 kJ.mol⁻¹ for Monomer **A** [57]. The rate of polymerization (R_p in units of fractional conversion per s) was calculated according to the following formula (Equation 3):

$$R_p = Q/(m \cdot \Delta H_{0p}) \text{ (Equation 3)}$$

where Q is the heat flow per unit time (in J.s⁻¹) during the reaction and m is the mass of the sample (in g). The rate of polymerization (R_p) and the double bond conversion (DBC) were plotted as a function of irradiation time.

2.3. Preparation of experimental SEA adhesives

Eight two-step SEP were studied using one of the four acid-based monomers (Monomers **A-D**) with either the CQ/EDAB or BAPO photo-initiator systems. Their compositions are detailed in Table 1. Comonomer mixtures were prepared from acidic monomers A-D (5 mol %) and DEBAAP (10 mol %). CH₂Cl₂ solutions of photoinitiator (camphorquinone, CQ), coinitiator (ethyl 4-(dimethylamino)benzoate, EDAB), and stabilizer (2,6-di-tert-butyl-4-methylphenol, BHT) were added via a microsyringe to give, after evaporation, the following final concentrations in the mixture: 1.0mol % CQ, 1.0 mol % EDAB, 0.03 mol % BHT. The remaining molar proportion of the adhesive system was a water/ethanol mixture with a 2/3 (v/v) ratio. A methacrylate monomer-based bonding resin (AdheSE bonding resin compound - bottle #2) was used as the second step. The resulting SEA systems were compared with a commercially available two-step SEA system (AdheSE, Ivoclar-Vivadent, Schaan, Liechtenstein).

Shear bond strength (SBS) of adhesive to dentin was assessed using the method described by the ISO/TS11405 standard. Ninety un-restored, caries-free, third human molars deemed suitable for testing were used within three months after extraction. The teeth were gathered following informed consent according to the protocols approved by the review board of the Dental Faculty of Paris Descartes University. The teeth were stored in 1% Chloramine T solution at 4 °C until used. Ten teeth were randomly assigned to each of the nine experimental groups. **SEP1-SEP8** are eight experimental primers (see table 1) composed of one acidic monomer chosen among compounds **A-D** (see Figure 2). These experimental

primers were compared amongst themselves and with a commercial resin AdheSE (Ivoclar-Vivadent, Schaan, Liechtenstein).

The occlusal surface of each tooth was ground under water on a Pedemax® polishing device (Struers A/S, Ballerup, Denmark) with #80 SiC paper to obtain a flat surface and expose middle dentin. The teeth were then embedded in cylindrical moulds using acrylic resin (Plexcil 6, Escil, Chassieu, France). The obtained samples were stored in water at 4 °C until used. Just before usage, the surface of the sample was ground with #800 SiC paper under water to expose a clean and flat dentin surface of suitable roughness.

The SEP were actively brushed onto the dentin surface with a regular size Microbrush® for 15 seconds. A waiting time of 15 seconds was respected before progressively air-drying the primers until sufficient ethanol diluent was evaporated so that no movement of the primer could be observed. Bonding resin was applied followed by air thinning for about 5 seconds. The primer and bonding resin (meaning the two parts of the SEAs) were then polymerized for 20 seconds using a LED curing unit (Radii Plus, Southern Dental Industries Ltd, Bayswater, Victoria, Australia). A Teflon® mould with a 3 mm cylindrical hole, 4 mm in height, was secured on the samples using a custom made aluminium device. The mold was filled with two increments of a dimethacrylate composite restorative (Z100® A3, 3M/ESPE, Saint-Paul, MN, USA). Each increment was light cured for 20 s. The irradiance of the LED curing unit was controlled with a radiometer (Cure Rite™, Dentsply Caulk, Milford, DE, USA) before each batch of sample and was greater than 1500 mW.cm⁻². After the mold parts were removed, samples consisting of embedded tooth with adhering dental composite were stored in deionized water at 37 °C for 24 hours prior to SBS testing. They were then shear loaded to fracture using a guillotine-type shearing device and a universal testing machine (Lloyd Instruments LRX, Ametek S.A.S., Elancourt, France) at a crosshead speed of 0.5 mm.min⁻¹.

The SBS results were statistically analyzed (IBM® SPSS® Statistics version 21, IBM Corporation, Armonk, NY, USA). Experimental formulations were tested pair-wise for monomer parameter effect using the Kruskal-Wallis non-parametric test.

The significance level was 0.05 for each test. In the statistical testing, the null hypothesis is that the bonding system has no effect.

3. Results

The photopolymerization behavior of DEBAAP with either the CQ/EDAB or BAPO photo-initiator system, as observed by DSC is shown in Figure 3. This data shows that BAPO polymerizes the DEBAAP monomer faster than the CQ/EDAB photoinitiation system, in that DEBAAP needs only 33 s to reach its maximum polymerization rate with BAPO and 73 s with CQ/EDAB system. The polymerization rate is further enhanced when an acid phosphonic acid monomer (Monomer A) is blended with DEBAAP for both photoinitiator systems. However, all systems appear to approach a final double bond conversion near 70%. The results of SBS tests are presented in Table 2. Adhesives based on phosphonic monomer (Monomer A) demonstrate results that are close ($p > 0.05$) to those obtained with AdheSE (Ivoclar-Vivadent, Schaan, Liechtenstein). More interestingly, adhesives based on phosphoric or dimethylfluorophosphonic monomers (Monomers B, C and D) provide better adhesion properties, showing their potential to constitute a good alternative to phosphonic acidic monomers.

4. Discussion

This study reports data from photo-DSC polymerizations performed under nitrogen conditions, and adhesive tests of the SEA-dentin bond strengths where the bonding procedure was carried out under an air atmosphere as would occur under clinical conditions. Therefore, an oxygen-induced retardation of the polymerization might be expected for the latter studies but the comparisons of the different formulations of the SEAs should be valid whatever the atmosphere.

4.1. Copolymerization of DEBAAP with CQ/EDAB and BAPO

In the first part of this study, we focused on the photopolymerization behavior of DEBAAP with either the CQ/EDAB or BAPO photo-initiator system. Figure 3 shows that BAPO polymerizes the monomer system faster than CQ/EDAB system and DEBAAP needs only 33 s to reach its maximum polymerization rate

with BAPO and 73 s with CQ/EDAB system. As BAPO is a Norrish I type initiator, the initiation is unimolecular. This fact partially explains why the reaction is faster when BAPO is used, however other factors such as the photon intensity in the two wavelength regions (360 and 410 nm) of the curing source, the absorption spectrum as well as the quantum efficiency of the photo-initiators and lastly, the number and efficiency of the formed radicals in initiating the polymerization are equally or more important. The higher photopolymerization rate can be an asset in the case of deep dental restoration because the gelation of the network-forming polymer will be faster, thus restricting oxygen diffusion earlier, and the depth of cure will be enhanced.[59-61]

In a previous paper [51], we discovered that the CQ/EDAB initiated polymerization of DEBAAP (difunctional acrylamide) was enhanced when an alkyl phosphonic acid species (either polymerizable or not) was added. This trend was surprising since the addition of a monofunctional monomer to a difunctional one should delay the onset of gelation and thus lead to a lower polymerization rate, and so the increased polarity of the medium by the phosphonic acid was advanced as the cause. Figure 3 confirms this result and shows that when the monomer **A** is added to a mixture composed of DEBAAP and CQ/EDAB, the system reaches a higher polymerization rate and it occurs at a shorter time (43 s of irradiation) than when DEBAAP and CQ/EDAB are used alone (73 s of irradiation).

Similar experiments were performed with BAPO, DEBAAP and monomer **A**. Once again, the incorporation of the monofunctional acrylamide **A** into the reaction medium leads to a lower time to reach the maximum polymerization rate (13 s for the mixture DEBAAP/**A** and 33 s for DEBAAP alone).

However, the effect of increased polarity brought by the phosphonic acid function on the reaction rate is not always observed. In a previous study of the polymerization of acrylamide and methacrylate monomers by the diphenyl iodonium hexafluorophosphate (Ph_2IPF_6) photo-initiator, the presence of alkyl phosphonic acids in the formulation reduced the polymerization rate due to an electrostatic interaction of the phosphonic acid moiety with the diphenyl iodonium cation.

Given the beneficial contribution of phosphonic acid monomers on the photopolymerization with either CQ/EDAB or BAPO, it was considered interesting to compare the dentine bonding strengths of DEBAAP-based primers formulated with both CQ/EDAB and BAPO initiators.

4.2. Adhesion tests

The second part of this paper is dedicated to the evaluation of the effect of BAPO or CQ/EDAB photo-initiator and of acidic monomers on the adhesion of different adhesive systems to dentine. The two-step self-etch adhesives were prepared from a series of experimental primers and were bonded to the dentine surface and then overlaid with a commercial bonding resin (AdheSE) followed by a dental composite restorative material (Z100®). Four different acidic monomers were investigated (see Figure 2). This study is based on the macro bonding test method because of its unrivalled ease and speed of use[62,63]. Monomer **A** is an acrylamidophosphonic acid with a 6-carbon alkyl chain between the vinyl and phosphonic acid groups already used in some of our previous study on dentin adhesion. This monomer has already demonstrated its high potential as a dental adhesive. Monomer **B** is an acrylamido(difluoromethyl)phosphonic acid with a 10-carbon alkyl spacer chain. This fluorinated phosphonic acid was selected because it is a methacrylate phosphonic acid analogue, Monomer **B**, is already known as a phosphate isosteric replacement group. As a consequence, Monomer **B** shows an adaptive chemical resemblance in particular, thanks to its close acidic constants (pK_a)[64]. This means that the behaviors of the two functions are the same regarding the chelation of cations as well as the interaction with binding sites of enzymes. In addition, Monomers **A** and **B** should exhibit high stability under acidic conditions which allow better performance of the corresponding adhesive. In contrast, Monomer **C** is likely to be less stable against hydrolysis due to its acrylamide moiety. The last monomer (Monomer **D**) contains both phosphate and methacrylate functions, and was included in the study because it is a well-studied monomer often known as 10-MDP (or **MDP**) commercialized by Kuraray since 1990 and used in a wide range of their

adhesives (such as Clearfil SE bond, Clearfil S³ bond). Although some studies[65] have shown this monomer to have good stability against hydrolysis due to its hydrophobic 10-carbon chain-length structure, the presence of the phosphate ester and the methacrylate ester moieties are expected to make them unstable under strong acidic conditions. As a reference adhesive system, we chose an adhesive commercialized by Ivoclar-Vivadent (Schaan, Liechtenstein) called AdheSE which is commonly used by dentists worldwide. According to its MSDS, this adhesive is composed of a CQ/EDAB initiating system and incorporates the monomer **E** (Figure 2) in its formulation.

The shear adhesive bonding experiments revealed that the majority of the failures were partly cohesive in the dentine rather than totally adhesive demonstrating the good adhesive properties of such adhesives to dentine. The adhesives **SEA1**, **SEA3**, **SEA5**, **SEA7** and the commercial system AdheSE are all based on the CQ/EDAB initiating system. The four experimental adhesive systems provide good results when monomers **A**, **B**, **C** or **D** (meaning **MDP**) are incorporated in the primer (Table 1 and 2). Nevertheless, the SBS values for adhesives **SEA5** and **SEA7** are greater and statistically different ($p<0.05$) than those of **SEA1** and **SEA3**, even though adhesives **SEA1** and **SEA3** are very close to the AdheSE ($p>0.05$).

The adhesives **SEA2**, **SEA4** and **SEA6** are all composed of primers based on BAPO as a photo-initiator. They appear to generally give higher SBS values than adhesives formulated with the CQ/EDAB system but results are not significantly different ($p>0.05$) except for adhesives **SEA3** versus **SEA4** ($p=0.03$), and for **SEA7** versus **SEA8** ($p<0.01$) which contain Monomers **B** and **D**, respectively. The reason for the difference in the results is not known.

A deeper penetration of BAPO in the dentin tubule due to its higher hydrophilic character and therefore a better surrounding of the collagen fibril leading to a deeper polymerization and a better protection of the dentin after surgery can explain these findings. It is well known that CQ is a hydrophobic photo initiator that might be either localized within hydrophobic phase or even incompatible with hydrophilic compounds.[64-67] Thus, for BAPO, a higher hardness is expected

than for CQ/EDAB system. Thus, DEBAAP is more likely to sub-optimally polymerize leading to a compromised final double bond conversion.

Regarding the pH effect of the primer on the bond strength, Table 1 shows that although Primers **SEP1** and **SEP2** have the lowest pH and are therefore more acidic, Table 2 reveals that when data for the same photoinitiation system are compared, better adhesion was generally found with Primers **SEP3-SEP8** which are less acidic. This result is contrary to expectations that a primer with a lower pH might provide stronger etching of the dentine and thus enhanced adhesion as well as a good bonding durability. Thus a treatment with phosphoric acid would be expected to etch the dental tissues very strongly whereas less acidic primers would be soft etching agents. Despite their lower etching capacity, the adhesion provided by primers with a higher pH (i.e., Primers **SEP3-SEP8**) can be explained by a better chelation of the calcium-containing hydroxyapatite according to the adhesion-decalcification concept proposed by Yoshida[68]. As a consequence, phosphoric acid Monomer **D** (i.e., **MDP**) and its fluorinated mimics[64] (i.e., Monomers **B** and **C**) allow a better demineralization than phosphonic acids leading to higher primer performance of the overall adhesive system. Moreover, monomer **D** and its phosphate mimics **B** and **C** should be able to create strong bonds with calcium from hydroxyapatite and therefore, more likely to avoid nanoleakage.

Table 2 also reveals that the the SBS obtained with adhesives based on phosphonic acid monomers were comparable to those obtained with the commercially available adhesive AdheSE (Ivoclar-Vivadent, Schaan, Liechtenstein).

CONCLUSION

This article demonstrates through a photo-DSC study the enhanced effect of phosphonic acid monomers on photopolymerization rate using the BAPO initiating system. It demonstrates also that this effect is not due to the initiating system since similar trends were noticed with the CQ/EDAB system as with BAPO.

Adhesion strength experiments to dentine were performed with several acidic monomers using CQ/EDAB or BAPO initiating systems. These results show similar levels of performance of the experimental primers compared with a commercial primer (AdheSE, Ivoclar-Vivadent, Schaan, Liechtenstein). The results also suggest a systematic enhanced performance of BAPO-based primers compared with CQ/EDAB based primers.

ACKNOWLEDGMENTS

This work was supported by EGIDE, Partenariat Hubert Curien French/Australian Science and Technology FAST2008 18603VH and FAST2010 23205WC grant and by the Australian Department of Innovation, Industry, Science and Research FR080034 and FR100037 grants, which provided funding for collaboration between the Laboratoire de Chimie Moléculaire et Thioorganique within the Institute of Chemistry INC3M FR 3038 and the “RMPP” (Réseau Matériaux, Polymères, Plasturgie) in France and the Department of Materials Engineering, Monash University in Australia. The authors thank Pr. Lequeux and Dr. A. Zulauf for providing fluorinated monomers B and C. The authors also gratefully acknowledge the financial support from the “Ministère de la Recherche et des Nouvelles Technologies,” CNRS (Centre National de la Recherche Scientifique), the “Région Basse- Normandie” and the European Union (FEDER funding) and the funding provided by the Australian Research Council for grant ARC DP1093217.A.

REFERENCES

- [1] Fouassier JP. Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications. Munich: Hanser Gardner Publications; 1995.
- [2] Photopolymerization: Fundamentals and Applications: American Chemical Society; 1997.
- [3] Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology. 2nd Edition ed: CRC Press; 2008.
- [4] Yeniad B, Albayrak AZ, Olcum NC, Avci D. Synthesis and photopolymerizations of new phosphonated monomers for dental applications. *Journal of Polymer Science Part A: Polymer Chemistry*. 2008;46:2290-9.
- [5] Catel Y, Degrange M, Le Pluart L, Madec P-J, Pham T-N, Picton L. Synthesis, photopolymerization and adhesive properties of new hydrolytically stable phosphonic acids for dental applications. *Journal of Polymer Science Part A: Polymer Chemistry*. 2008;46:7074-90.
- [6] Catel Y, Degrange M, Pluart LL, Madec P-J, Pham T-N, Chen F, et al. Synthesis, photopolymerization, and adhesive properties of new bisphosphonic acid monomers for dental application. *Journal of Polymer Science Part A: Polymer Chemistry*. 2009;47:5258-71.
- [7] Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A, et al. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials*. 2007;28:3757-85.
- [8] Moszner N, Salz U, Zimmermann J. Chemical aspects of self-etching enamel-dentin adhesives: a systematic review. *Dental materials : official publication of the Academy of Dental Materials*. 2005;21:895-910.
- [9] Schwarzenbach G, Ackermann H, Ruckstuhl P. Komplexe XV. Neue Derivate der Imino-diessigsäure und ihre Erdalkalikomplexe. Beziehungen zwischen Acidität und Komplexbildung. *Helvetica Chimica Acta*. 1949;32:1175-86.
- [10] Nakabayashi N, Pashley DH. Hybridization of Dental Hard Tissues. Tokyo: Quintessence publishing; 1998.
- [11] Ikemura K, Tay FR, Nishiyama N, Pashley DH, Endo T. Multi-purpose Bonding Performance of Newly Synthesized Phosphonic Acid Monomers. *Dental Materials Journal*. 2007;26:105-15.
- [12] Sahin G, Albayrak AZ, Bilgici ZS, Avci D. Synthesis and evaluation of new dental monomers with both phosphonic and carboxylic acid functional groups. *Journal of Polymer Science Part A: Polymer Chemistry*. 2009;47:1953-65.
- [13] Derbanne M, Besse V, Le Goff S, Attal J-P, Pham T-N, Degrange M. Synthesis and adhesive properties of acidic monomers for dental applications. *Dental materials : official publication of the Academy of Dental Materials*. 2010;e6.
- [14] Breschi L, Mazzoni A, Ruggeri A, Cadenaro M, Di Lenarda R, De Stefano Dorigo E. Dental adhesion review: aging and stability of the bonded interface. *Dental materials : official publication of the Academy of Dental Materials*. 2008;24:90-101.
- [15] De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, et al. A Critical Review of the Durability of Adhesion to Tooth Tissue: Methods and Results. *Journal of Dental Research*. 2005;84:118-32.

- [16] Bayle MA, Gregoire G, Sharrock P. The role of acrylophosphonic acid monomers in the formation of hybrid layers based on self-etch adhesives. *Journal of dentistry*. 2007;35:302-8.
- [17] Bayle MA, Nasr K, Gregoire G, Sharrock P. Acrylophosphonic acid reactivity with calcium ions and biological apatite. *Dental materials : official publication of the Academy of Dental Materials*. 2008;24:386-91.
- [18] Van Landuyt KL, Yoshida Y, Hirata I, Snauwaert J, De Munck J, Okazaki M, et al. Influence of the Chemical Structure of Functional Monomers on Their Adhesive Performance. *Journal of Dental Research*. 2008;87:757-61.
- [19] Flory P. *Principles of polymer chemistry*: Cornell University Press; 1953.
- [20] Cook WD. Thermal aspects of the kinetics of dimethacrylate photopolymerization. *Polymer*. 1992;33:2152-61.
- [21] Dvorni PR, Jacovic MS. The viscosity effect on autoacceleration of the rate of free radical polymerization. *Polymer Engineering and Science*. 1981;21:792-6.
- [22] Hayden P, Melville H. The kinetics of the polymerization of methyl methacrylate. II. The crosslinked and heterogeneous reaction. *Journal of Polymer Science*. 1960;43:215-27.
- [23] Scott TF, Cook WD, Forsythe JS. Photo-DSC cure kinetics of vinyl ester resins. I. Influence of temperature. *Polymer*. 2002;43:5839-45.
- [24] Landin D, Macosko C. Cyclization and reduced reactivity of pendant vinyls during the copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. *Macromolecules*. 1988;21:846-51.
- [25] Cook WD. Spectral Distributions of Dental Photopolymerization Sources. *Journal of Dental Research*. 1982;61:1436-8.
- [26] Jakubiak J, Allonas X, Fouassier JP, Sionkowska A, Andrzejewska E, Linden LÅ, et al. Camphorquinone–amines photoinitiating systems for the initiation of free radical polymerization. *Polymer*. 2003;44:5219-26.
- [27] 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. *European journal of oral sciences*. 2004;112:280-5.
- [28] Asmussen E. Clinical relevance of physical, chemical, and bonding properties of composite resins. *Oper Dent*. 1985;10:61-73.
- [29] Asmussen S, Arenas G, Cook WD, Vallo C. Photoinitiation rate profiles during polymerization of a dimethacrylate-based resin photoinitiated with camphorquinone/amine. Influence of initiator photobleaching rate. *European Polymer Journal*. 2009;45:515-22.
- [30] Nomura Y, Teshima W, Kawahara T, Tanaka N, Ishibashi H, Okazaki M, et al. Genotoxicity of dental resin polymerization initiators in vitro. *Journal of materials science Materials in medicine*. 2006;17:29-32.
- [31] Weisburger E, Russfield A, Homburger F, Weisburger J, Boger E, Van Dongen C. Testing of twenty-one environmental aromatic amines or derivatives for long-term toxicity or carcinogenicity. *J Environ Pathol Toxicol*. 1979;2:325-56.
- [32] Ilie N, Hickel R. Can CQ Be Completely Replaced by Alternative Initiators in Dental Adhesives? *Dental Materials Journal*. 2008;27:221-8.
- [33] Schneider LF, Cavalcante LM, Prahl SA, Pfeifer CS, Ferracane JL. Curing efficiency of dental resin composites formulated with camphorquinone or trimethylbenzoyl-diphenyl-phosphine oxide. *Dental materials : official publication of the Academy of Dental Materials*. 2012;28:392-7.

- [34] Stansbury JW. Curing Dental Resins and Composites by Photopolymerization. *Journal of Esthetic and Restorative Dentistry*. 2000;12:300-8.
- [35] Suh BI. Controlling and understanding the polymerization shrinkage-induced stresses in light-cured composites. *Compendium of continuing education in dentistry*. 1999;20:S34-41.
- [36] Park YJ, Chae KH, Rawls HR. Development of a new photoinitiation system for dental light-cure composite resins. *Dental Materials*. 1999;15:120-7.
- [37] Burtscher P, Rheinberger V. Efficiency of Various Light Initiators after Curing with Different Light-curing Units. *J dent res*. 2003;81.
- [38] Sun GJ, Chae KH. Properties of 2,3-butanedione and 1-phenyl-1,2-propanedione as new photosensitizers for visible light cured dental resin composites. *Polymer*. 2000;41:6205-12.
- [39] Scott TF, Cook WD, Forsythe JS, Bowman CN, Berchtold KA. FTIR and ESR spectroscopic studies of the photopolymerization of vinyl ester resins. *Macromolecules*. 2003;36:6066-74.
- [40] Ikemura K, Endo T. A review of the development of radical photopolymerization initiators used for designing light-curing dental adhesives and resin composites. *Dental Materials Journal*. 2009;29:481-501.
- [41] Jockusch S, Koptug IV, McGarry PF, Sluggett GW, Turro NJ, Watkins DM. A Steady-State and Picosecond Pump-Probe Investigation of the Photophysics of an Acyl and a Bis(acyl)phosphine Oxide. *Journal of the American Chemical Society*. 1997;119:11495-501.
- [42] Sumiyoshi T, Schnabel W, Henne A, Lechtken P. On the photolysis of acylphosphine oxides: 1. Laser flash photolysis studies with 2,4,6-trimethylbenzoyldiphenylphosphine oxide. *Polymer*. 1985;26:141-6.
- [43] Rueggeberg FA, Ergle JW, Lockwood PE. Effect of photoinitiator level on properties of a light-cured and post-cure heated model resin system. *Dental Materials*. 1997;13:360-4.
- [44] Studer K, Königer R. Initial photoyellowing of photocrosslinked coatings. *Eur Coat J*. 2001;1:26-37.
- [45] Arikawa H, Takahashi H, Kanie T, Ban S. Effect of various visible light photoinitiators on the polymerization and color of light-activated resins. *Dental Materials Journal*. 2009;28:454-60.
- [46] Lee JW, Ahn G, Kim DS, Cho D-W. Development of nano- and microscale composite 3D scaffolds using PPF/DEF-HA and micro-stereolithography. *Microelectronic Engineering*. 2009;86:1465-7.
- [47] Schuster M, Turecek C, Varga F, Lichtenegger H, Stampfl J, Liska R. 3D-shaping of biodegradable photopolymers for hard tissue replacement. *Applied Surface Science*. 2007;254:1131-4.
- [48] Anido-Anido A, Souza-Junior E, Brandt W, Nogueira Leal Silva E, Alonso R, Zaia A, et al. Dental adhesives containing alternative photoinitiators: Degree of conversion and cytotoxicity. *Dental materials : official publication of the Academy of Dental Materials*. 2012;28.
- [49] Allen NS. Photoinitiators for UV and visible curing of coatings: Mechanisms and properties. *Journal of Photochemistry and Photobiology A: Chemistry*. 1996;100:101-7.

- [50] Rutsch W, Dietliker K, Leppard D, Köhler M, Misev L, Kolczak U, et al. Recent developments in photoinitiators. *Progress in Organic Coatings*. 1996;27:227-39.
- [51] Besse V, Le Pluart L, Cook WD, Pham TN, Madec PJ. Synthesis and polymerization kinetics of acrylamide phosphonic acids and esters as new dentine adhesives. *Journal of Polymer Science Part A: Polymer Chemistry*. 2013;51:149-57.
- [52] Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. *Biomaterials*. 2002;23:1819-29.
- [53] Besse V, Le Pluart L, Cook WD, Pham T-N, Madec P-J. Polymerization kinetics of phosphonic acids and esters using an iodonium initiator. *Journal of Polymer Science Part A: Polymer Chemistry*. 2013;51:5046-55.
- [54] Cook WD. Photopolymerization kinetics of oligo(ethylene oxide) and oligo(methylene) oxide dimethacrylates. *Journal of Polymer Science Part A: Polymer Chemistry*. 1993;31:1053-67.
- [55] Cook WD. Photopolymerization kinetics of dimethacrylates using the camphorquinone/amine initiator system. *Polymer*. 1992;33:600-9.
- [56] Klee JE, Lehmann U. N-alkyl-N-(phosphonoethyl) substituted (meth)acrylamides - new adhesive monomers for self-etching self-priming one part dental adhesive. *Beilstein journal of organic chemistry*. 2009;5:72.
- [57] Gómez MaL, Avila V, Montejano HA, Previtali CM. A mechanistic and laser flash photolysis investigation of acrylamide polymerization photoinitiated by the three component system safranin-T/triethanolamine/diphenyliodonium chloride. *Polymer*. 2003;44:2875-81.
- [58] Joshi RM. Heats of polymeric reactions. Part I. Construction of the calorimeter and measurements on some new monomers. *Journal of Polymer Science*. 1962;56:313-38.
- [59] Cook WD. Depth of Cure in the UV Photopolymerization of Dimethacrylate-Based Dental Filling Materials. *Journal of Macromolecular Science: Part A - Chemistry*. 2006;17:99-111.
- [60] Cook WD, Standish PM. Cure of resin based restorative materials. II. White light photopolymerized resins. *Australian Dental Journal*. 1983;28:307-11.
- [61] Teshima I. Degradation of 10-methacryloyloxydecyl dihydrogen phosphate. *J Dent Res*. 2010;89:1281-6.
- [62] Burke FJT, Hussain A, Nolan L, Fleming GJP. Methods used in dentine bonding tests: An analysis of 102 investigations on bond strength. *Eur J Prosthodont Rest Dent* 2008;16:158-165.
- [63] Salz U, Bock T. Testing Adhesion of Direct Restoratives to Dental Hard Tissue – A Review. *J. Adhes. Dent*. 2010;12:343-371.
- [64] Chambers RD, Jaouhari R, O'Hagan D. Fluorine in enzyme chemistry. Part 1: The preparation of difluoromethylphosphonate analogues of glycolytic phosphates. Approaching an isosteric and isoelectronic phosphate mimic. *J. Fluorine Chem*. 1989; 44: 275-284.
- [65] Wang Y, Spencer P, Yao X, Ye Q. Effect of coinitiator and water on the photoreactivity and photopolymerization of HEMA/camphorquinone-based reactant mixtures. *Journal of biomedical materials research Part A*. 2006;78:721-8.

- [66] Guo X, Wang Y, Spencer P, Ye Q, Yao X. Effects of water content and initiator composition on photopolymerization of a model BisGMA/HEMA resin. *Dental materials* : official publication of the Academy of Dental Materials. 2008;24:824-31.
- [67] Cadenaro M, Antonioli F, Codan B, Agee K, Tay FR, Dorigo Ede S, et al. Influence of different initiators on the degree of conversion of experimental adhesive blends in relation to their hydrophilicity and solvent content. *Dental materials* : official publication of the Academy of Dental Materials. 2010;26:288-94.
- [68] Yoshida Y, Van Meerbeek B, Nakayama Y, Yoshioka M, Snauwaert J, Abe Y, et al. Adhesion to and decalcification of hydroxyapatite by carboxylic acids. *J Dent Res*. 2001;80:1565-9.

TABLES

Compounds	Primer SEP1	Primer SEP2	Primer SEP3	Primer SEP4	Primer SEP5	Primer SEP6	Primer SEP7	Primer SEP8
Monomer A	20.53	20.5	-	-	-	-	-	-
Monomer B	-	-	26.1	26.05	-	-	-	-
Monomer C	-	-	-	-	26.21	26.15	-	-
Monomer D	-	-	-	-	-	-	24.6	24.96
DEBAAP	39.28	39.14	36.17	36.11	36.49	36.41	36.44	36.47
Water	15.72	15.75	14.7	14.67	14.62	14.58	14.65	14.65
Ethanol	23.58	23.63	22.2	22.16	21.88	21.82	22.9	22.91
CQ	0.38	-	0.35	-	0.36	-	0.64	-
EDAB	0.48	-	0.45	-	0.41	-	0.74	-
BAPO	-	0.98	-	0.98	-	1	-	0.98
BHT	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
pH	1.77	1.77	2.21	2.21	2.46	2.46	2.65	2.65

Table 1: Compositions (wt %) and pH of the experimental **SEP1** to **SEP8**. These figures are based on molar compositions of 10 mol % DEBAAP monomer, 5 mol % phosphonate monomer, 1 mol % CQ, 1 mol % EDAB, 0.03 mol % BHT and with the remainder being a water/ethanol mixture with a 2/3 (v/v) ratio.

Adhesive	SEA1^{a,c}	<u>SEA2</u>^a	SEA3^{b,c}	<u>SEA4</u>^b	SEA5^a	<u>SEA6</u>^b	SEA7^{b,c}	<u>SEA8</u>^b	AdheSE ^c
Mean SBS (MPa)	15.2	19.0	14.0	22.8	24.2	27.6	17.9	25.0	13.8
S.D.	3.2	3.0	2.9	3.8	6.2	3.2	3.8	3.1	2.4

Table 2: Adhesion shear bond strengths for adhesives **SEA1** to **SEA8** and AdheSE (Primers containing BAPO have their names underlined). Non statistically different samples are presented with an identical letter in superscript. A significance level of 5% was chosen.

CAPTIONS

Figure 1: Homolytic α -cleavage of bis(acyl)phosphine oxide (BAPO) under light irradiation

Figure 2: Structures of monomers and initiators used in this study

Figure 3: Fractional conversion rate and fractional conversion of double bonds versus irradiation time for the homopolymerization of DEBAAP and monomer A with CD/EDAB and BAPO initiating system. Irradiation of the samples commenced at 60 s.

Figure 1: Homolytic α -cleavage of bis(acyl)phosphine oxide (BAPO) under light irradiation

Figure 2: Structures of these monomers and initiators used in this study

Figure 3: Fractional conversion rate (R_p) and fractional conversion of double bonds versus irradiation time for the homopolymerization of DEBAAP and monomer A with CD/EDAB and BAPO initiating system.