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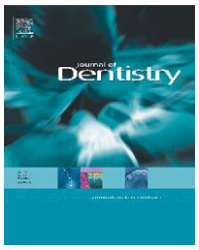

Effect of proanthocyanidins and photo-initiators on photo-polymerization of a dental adhesive

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ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form
26 September 2012
Accepted 6 October 2012

Keywords:
Dental adhesive
Proanthocyanidins
Degree of conversion
ATR-FTIR

ABSTRACT

Objectives: To evaluate the effects of proanthocyanidins (PA) and photoinitiator type on the degree of conversion (DC) and polymerization rate (PR) of a model dental adhesive.
Methods: Three types of photo-initiation systems were introduced into the Bis-GMA/HEMA co-monomer mixture, resulting in four resin formulations including CQ/A (0.5 wt% CQ and EDMAB), CQ/A/I-1 (0.5 wt% CQ, EDMAB and DPIHP), CQ/A/I-2 (1.0 wt% CQ, EDMAB and DPIHP), and TPO (2.1 wt% TPO). For each resin formulation, adhesives containing 0%, 2.5%, 5% and 10% of PA with respect to the weight of resin were produced after mixing the resin with various amount of PA/ethanol solution. When light-cured, the RP and DC of each adhesive was determined using ATR-FTIR spectroscopy.
Results: Across and within the initiator groups, the DC followed the general trend of CQ/A < CQ/A/I-1 < CQ/A/I-2 < TPO and 0-PA > 2.5-PA > 5-PA > 10-PA, respectively. The change of PR with respect to photo-initiation systems and PA content was in a similar but less pronounced pattern.
Conclusion: PA hampered the polymerization of all adhesives regardless of photoinitiators used. The initiator formulations CQ/A/I-2 and TPO are better fit for PA-containing adhesives, both leading to >65% DC in the presence of 5% PA.
Clinical significance: The inclusion of PA in dental adhesives has been limited by its interference with the light-curing of adhesive resins. This study found photo-initiation formulations that could maintain a satisfactory degree of monomer conversion while a significant amount of PA is incorporated.

1. Introduction

Composite dental fillings were first introduced into the field of restorative dentistry in the 1960s.[1] Despite over 50 years of development, the durability of composite restorations is still no match to that of the traditional amalgam fillings.[2,3] One of the leading causes for the failure of composite fillings is the loss of marginal integrity,[3,4] suggesting that the composite-dentin interface is a major issue. While the use of dental adhesives has greatly improved the interfacial strength in the short term,[5] its long-term stability leaves a lot to be desired. The basis for adhesives' bonding is the adhesive/dentin hybrid layer, which is composed of adhesive polymers and demineralized collagen fibrils that form micro-interlocked entanglement.[6] Unlike mineralized collagen fibrils found in the intact dentin, collagen fibrils in the hybrid layer are partially exposed due to a number of reasons such as the incomplete resin infiltration and unsatisfactory degree of polymerization.[7,8] As a result, collagen fibrils in the hybrid layer are vulnerable to

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0300-5712/$ – see front matter
http://dx.doi.org/10.1016/j.jdent.2012.10.006

hydrolytic and enzymatic degradation, which could in turn contributes to the breakdown of the dentin-composite interface. In addition, recent studies have revealed that the acid etching of dentin activates the otherwise dormant host-derived matrix metalloproteinases (MMPs),[9] further increasing the risk of collagen degradation. Based on the above information, the importance of exploring materials and techniques to enhance dentin collagen's biological stability becomes self-evident.

One common practice to improve collagen's resistance toward hydrolytic and enzymatic degradation is to treat it with cross-linking agents. Indeed, a number of studies have established that dentin collagen presented enhanced mechanical and biological properties upon cross-linking.[10–17] Among all the cross-linking agents reported, a group of naturally occurring polyphenolic compounds, proanthocyanidins (PA) is of particular interest, because not only is it highly efficient in cross-linking collagen, it is also non-toxic and readily available.[18,19] As such, it is warranted to investigate the effect of PA on the performance of current dental adhesive systems, and to design an optimal approach for its use.

There are two options when incorporating PA in an adhesive system: as a primer, or as an additive to the adhesive. In the former approach, PA is applied and rinsed off prior to the application of adhesive, and therefore has little to no effect on the light-curing of adhesive resin. The limitation of this approach is the time constraint when applying PA as a primer, as well as the lack of sustained release of PA to exert its protective effect on dentin collagen over a long time period. The reported application time varied from 10 min to 1 h, which is not feasible in clinical setting.[10–14] In comparison, the latter approach could afford a sustained release of PA, but the presence of PA during light-curing might interfere with polymerization of adhesive monomers. After all, PA is a known radical scavenger,[19] and it is only natural to anticipate that such radical-consuming capability could be detrimental to the light-curing process which relies on the generation and propagation of radical species to make the resin set. In addition, the release of PA could lead to resin breakdown and reduce integrity of the bonding interface when the resin is poorly cured.

Not surprisingly, when Green et al.[13] examined the hybrid layer formed with PA-containing adhesives, they found that it presented more porous morphology as compared to its PA-free counterpart, presumably due to a lower degree of conversion of adhesive resins. In addition, Hechler et al.[20] examined both approaches as stated above, they found that when PA was directly mixed with the adhesive, the microtensile bond strength was lower than when PA was used as a primer after one year of collagenase digestion. In another study,[21] Epasinghe et al. also reported a lower bond strength when a higher dose of PA was included in the adhesive. These results, however, are still circumstantial evidences that PA might adversely interfere with the radical polymerization of dental adhesives. Consequently, this work aimed to directly study dental resin's polymerization behavior as a function of PA concentration and different initiator system. By examining the degree of conversion (DC) and polymerization rate (PR) of PA-containing model adhesive upon light-curing, the null hypothesis tested was that the polymerization behavior of the adhesive is not affected by the presence of PA or photo-initiator system used.

2. Materials and methods

2.1. Reagents

Bisphenol A glycidyl dimethacrylate (Bis-GMA), 2-hydroxyethyl methacrylate (HEMA), camphorquinone (CQ), trimethylbenzoyl-diphenylphosphine oxide (TPO), ethyl (4-dimethyl amino) benzoate (EDMAB), diphenyliodonium hexafluorophosphate (DPIHP) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Ethanol was purchased from Pharmco-AAPER (Brookfield, CT, USA). Grape seed extract proanthocyanidin (PA) was generously donated by MegaNatural (Madera, CA, USA). All reagents were used as received.

2.2. Formulation of PA-containing model adhesives

Model adhesives with compositions similar to commercial dental adhesives such as Single Bond were used in the presented research.[13] The protocol involved the preparation of a photo-initiator-containing neat resin and a PA-containing ethanol solution prior to mixing them together to make the final PA-containing model adhesive. The neat resin consisted of Bis-GMA and HEMA at a Bis-GMA/HEMA mass ratio of 55/45. Three CQ-based photo-initiator formulations (CQ/A, CQ/A/I-1 and CQ/A/I-2), and one TPO-based formulation (TPO) were added to the neat resin at selected concentrations as shown in Table 1. Specifically, CQ/A is a traditional two-component CQ-based initiator system with tertiary amine (A) EDMAB as the co-initiator, CQ/A/I-1 is a three-component system with extra iodonium salt (I) DPIHP, CQ/A/I-2 shares the same composition as CQ/A/I-1 but with twice the amount of initiators, and TPO is a single-component system with TPO at the same molar concentration as CQ in CQ/A/I-2. Each of the four resultant initiator-containing neat resins was then mixed with 0% (w/w), 3.75% (w/w), 7.5% (w/w), and 15% (w/w) PA/ethanol solution, respectively, at a resin/solution mass ratio of 60/40. This concluded the formulation of the control pure adhesive (0-PA), as well as adhesives containing 2.5% (2.5-PA), 5% (5-PA), and 10% of PA (10-PA) with respect to the mass of neat resins. All adhesive samples were prepared in a room with amber lights, and vortexing and sonication were required to ensure solutions to be well-mixed.

Table 1 – Formulations of the four photoinitiators studied (weight with respect to Bis-GMA/HEMA resin).

Denotation	Components			
	CQ (wt%)	EDMAB (wt%)	DPIHP (wt%)	TPO (wt%)
CQ/A	0.5	0.5	–	–
CQ/A/I-1	0.5	0.5	0.5	–
CQ/A/I-2	1.0	1.0	1.0	–
TPO	–	–	–	2.1