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Hydrolytically stable acidic monomers used in two steps self-etch adhesives

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ABSTRACT

This study deals with the stability of new phosphonic monomers bearing an acrylamide moiety designed to increase the adhesion durability. Synthesis of monomers bearing acrylamide and methacrylate moieties, as well as their use in Self-Etch Adhesives is reported. The adhesion of a degraded methacrylate based adhesive has been evaluated. Homologous self-etching primers containing monomers bearing acrylamide or methacrylate were formulated and used either immediately after formulation or after 18 months. Their adhesive performances were assessed by shear bond strength testing and their degradation measured by NMR, HPLC-MS. While no differences were found in terms of adhesion between fresh and aged acrylamide based adhesive, the instability of methacrylate based ones was demonstrated. Nevertheless, methacrylate based SEAs still have good adhesion abilities. The co-monomer used, *N,N′*-diethyl-1,3-bis(acrylamido)propane is expected to be responsible for good mechanical properties even for degraded SEAs. Lastly, the stability of acrylamide monomer seems to be of interest in the prospect of developing SEA with longer shelf life.

1. Introduction

Dental adhesive systems mediate the bond between tooth substrate (dentin or enamel) and restorative materials. Amongst the currently available adhesive systems, two-steps self-etching adhesive (SEA) systems combine etching and priming into one step and do not require rinsing. The apparent user-friendliness of these materials has greatly improved their development and popularity [1–3]. These systems contain a self-etching primer (SEP) that needs to be able to etch enamel and dentin in order to promote the infiltration of the bonding resin into the etched/demineralized substratum allowing for micromechanical retention after polymerization of the resin. These requirements are achieved by using derivative of methacrylic acid monomers, which may contain carboxylic, phosphate, sulfonic, or phosphonic moieties [4]. SEP usually have a pH value between 1 and 5 and can contain up to 40% water [1,5,6]. Under such acidic conditions, most of the employed monomers [usually (meth)acrylates] are not stable and undergo hydrolysis during storage, resulting in the potential loss of their bonding ability [7–9].

Some acidic monomers with stability against hydrolysis have been proposed [8–12]. Hydrolytically stable cross-linking monomers have also been described [8,9,12,13]. While more hydrolytically stable than esters because of the lower reactivity of their carbonyl groups, these acrylamide based compounds are not perfectly stable under strong acidic conditions. However, drastic conditions and strong catalysts such as concentrated sulfuric or phosphoric acid are often needed to effect hydrolysis [13]. Their near perfect stability while used as dental adhesive component has already been proven [9,11,12].

However, there is a scarcity of scientific papers dealing with them and their impact on adhesive performance. Furthermore, the comparison between hydrolysis-prone adhesive systems and stable ones had usually been assessed with commercially available systems of various proprietary compositions.

In this context, we developed two-step SEA composed of experimental (acrylamido) and (methacryloyloxy)phosphonic acid based SEP used in conjunction with a commercially available bonding resin

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to investigate their bonding stability during prolonged storage. As a control, a simulated 100% degraded methacryloyloxy based SEP was also prepared.

The null hypothesis was that acidic monomer degradation does not affect immediate bond strength of experimental two-steps SEA.

2. Experimental – part 1. Synthesis and storage stability

2.1. Materials

Triethylamine was distilled over calcium hydride prior to use. Unless stated otherwise, all reagents were purchased from Sigma–Aldrich (Sigma–Aldrich SARL, Lyon, France) and were used without further purification. *N*,*N*′-diethyl-1,3-bis(acrylamido)propane (DEBAAP) was prepared according to the literature [13]. Dichloromethane was purified with a Puresolv™ apparatus (Innovative Technology, Newburyport, MA, USA). Column chromatography was performed on silica gel Si 60 (40–63 μm). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Merck Chemicals, Darmstadt, Germany). All reactions were carried out under a dry nitrogen atmosphere in oven-dried glassware.

2.2. Measurements

Each synthesized product was characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and by high-resolution mass spectroscopy (HRMS). The ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a 400 MHz AC 400 spectrometer (Brucker Optics GmbH, Ettlingen, Germany), with TMS as internal reference for ^{1}H NMR and ^{13}C NMR chemical shifts, and with H_3PO_4 (85%) as external reference for ^{31}P NMR chemical shifts. High-resolution mass spectra were obtained with a Q-TOF Micro instrument (Waters Corporation, Milford, MA, USA) in electrospray ionization positive (ES+) or negative (ES−) mode and lockspray with orthophosphoric acid. These analyses were performed with an infusion introduction of 10 μL min^{-1}, a source temperature of 80 °C, a desolvation temperature of 120 °C and an external calibration with NaI. A Waters Alliance/Q-TOF Micro system was employed for the determination of the analytes of interest, which consisted of an Alliance 2695 Separation Module system (Waters Corp., Milford, MA, USA) with cooling autosampler, column oven and a Waters 2996 Photodiode Array Detector, and a Q-TOF Micro mass spectrometric detection with an electrospray ionization (ESI) interface (Waters Corp., Milford, MA, USA). A Waters XTERRA MS C18 column (150 mm × 4.6 mm, 3.5 μm, Waters Corp., Milford, MA, USA) was used to separate the analytes. All data were acquired and processed using MassLynx 4.1 software (Waters Corp., Milford, MA, USA). An isocratic elution programme was conducted for chromatographic separation with the mobile phase A (acetonitrile), and the mobile phase B (water) as follows: 40% A, 60% B (v/v). The flow rate was 0.5 mL/min and column temperature was 35 °C. Injection wash solvent was methanol. For MS detection, positive and negative ESI were used as the ionization mode. Nitrogen was used as the desolvation and cone gas with a flow rate of 600 and 50 L/h, respectively. The optimal MS parameters were as follows: capillary 3 kV for positive ESI and 3.5 kV for negative ESI, source temperature 120 °C and desolvation temperature 400 °C. Cone voltage was 30 V. The pH measurements were performed at room temperature (22 °C) with a contact electrode (PHC2441-8 Combined pH Electrode "Red Rod") with a PHM210 Standard pH Meter (Radiometer Analytical, Villeurbanne, France).

2.3. Preparation of experimental SEA adhesives

Two-steps experimental SEA systems employed were made of three different experimental SEP used in conjunction with one bonding resin of a commercially available two steps SEA system (AdheSE, Ivoclar-Vivadent, Schann, Liechtenstein). The description of the chemical species used and the compositions of the formulations are detailed respectively in Tables 1 and 2.

The phosphonic acid monomer used for the acrylamide batches (**FreshA** and **AgedA**) was 10-(*N*-methylacrylamido)decylphosphonic acid **10** (**MonoA**). Synthesis of this monomer was previously described [8].

The homologous methacrylate monomer (used for groups **FreshM** and **AgedM**), was 10-(methacryloyloxy)decylphosphonic acid **5** (**MonoM**).

Synthesis of the simulated 100% degraded monomer was also carried out. Methacrylate based monomer are known to undergo hydrolysis in acidic aqueous conditions leading to the transformation of the monomer into methacrylic acid (**MonoDA**) which is commercially available and an alcohol carrying the functional group of the degraded monomer **6** (**MonoDB**). Mixture of **MonoDA** and **MonoDB** was used to formulate a totally degraded SEP (**Deg**).

Structures and syntheses are presented respectively in Figs. 1–3.

2.4. Syntheses

2.4.1. 2-(10-bromodecyloxy)tetrahydro-2H-pyrane **1**

10-Bromodecanol (6.5 g, 27.6 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (72.0 mg, 0.3 mmol) diluted in anhydrous dichloromethane (30 mL) were introduced in a round bottom flask. Then dihydropyrane (6.2 g, 27.6 mmol, 1 equiv) was added and the mixture was stirred for 3 h at room temperature. The crude was washed with distilled water (50 mL). The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. A bulb to bulb distillation under reduced pressure provided the pure product (5.85 g, 18.2 mmol) as colorless oil.

Yield: 66%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 1.25–1.86 (m, 22H, H_2–H_9 and H_{13}–H_{15}), 3.35–3.42 (m, 2H, H_{10}), 3.39–3.42 (t, ^{3}J = 4.4 Hz, 2H, H_1), 3.70–3.90 (m, 2H, H_{12}), 4.57 (t, ^{3}J = 2.8 Hz, 1H, H_{11}). ^{13}C NMR ($CDCl_3$, 101 MHz, δ): 19.8 (s, C_{14}), 25.6 (s, C_2), 26.3 (s, C_{13}), 28.3 (s, C_1), 28.8 (s, C_4), 29.4 (s, C_5), 29.5 (s, C_9), 29.6 (s, C_6) 29.9 (s, C_7), 30.9 (s, C_4), 32.9 (s, C_3), 34.2 (s, C_{15}), 62.5 (s, C_{10}), 67.8 (s, C_{12}), 90.0 (s, C_{11}). HRMS (*m*/*z*): calcd for $C_{15}H_{29}O_2NaBr$, 343.1249; found, 343.1241 $[M + Na]^+$.

2.4.2. Diethyl 10-(tetrahydropyran-2-yloxy)decylphosphonate **2**

Acetal **1** (4.6 g, 14.3 mmol) and triethylphosphite [$P(OEt)_3$] (6.2 mL, 35.8 mmol, 2.5 equiv) were introduced in a round-bottom flask, then the mixture was heated at 150 °C for 15 h. Excess of triethylphosphite and side products were eliminated *via* a bulb to bulb distillation to give the pure product (4.6 g, 12.7 mmol) as colorless oil.

Yield: 89%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 1.26–1.32 [m, 10H, H_3–H_8 and C**H**$_3$(OEt)], 1.47–1.58 (m, 4H, H_9 and H_2), 1.63–1.70 (m, 6H, H_{13}–H_{15}); 3.33–3.51 (m, 2H, H_{10}), 3.68–3.87 (m, 2H, H_1), 4.02–4.13 [m, 6H, H_{12} and C**H**$_2$(OEt)], 4.57–4.60 (m, 1H, H_{11}). ^{13}C NMR ($CDCl_3$, 101 MHz, δ): 16.6 [d, $^{3}J_{CP}$ = 6.0 Hz, **C**H_3(OEt)], 19.8 (s, C_{14}), 22.5 (d, $^{2}J_{CP}$ = 5.2 Hz, C_2), 25.6 (s, C_{13}), 25.8 (d, $^{1}J_{CP}$ = 140.4 Hz, C_1), 26.3 (s, C_4), 29.2 (s, C_5), 29.4 (s, C_9), 29.5 (s, C_6) 29.6 (s, C_7), 29.8 (s, C_4), 30.7 (d, $^{3}J_{CP}$ = 17.0 Hz, C_3), 30.9 (s, C_{15}), 61.5 [d, $^{2}J_{CP}$ = 6.5 Hz, **C**H_2(OEt)], 62.4 (s, C_{10}), 67.8 (s, C_{12}), 98.9 (s, C_{11}). ^{31}P NMR ($CDCl_3$, 162 MHz, δ) = 32.7. HRMS (*m*/*z*): calcd for $C_{19}H_{40}O_5P$, 379.2613; found, 379.2615 $[M + H]^+$.

2.4.3. Diethyl 10-hydroxydecylphosphonate **3**

Diethyl 10-(tetrahydropyran-2-yloxy)decylphosphonate **2** (1.0 g, 2.7 mmol) and Amberlyst H15 (100 mg) were introduced in a round-bottom flask with methanol (MeOH) (5 mL). The reaction was