Tertiary Amine and Tooth Mineral Hydroxyapatite Facilely Trigger Self-cure of 10-MDP Based Adhesives

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Abstract

The present work aims to investigate if a novel self-cure system, mediated by tertiary amine ethyl 4-(dimethylamino)-benzoate (4E) and tooth mineral hydroxyapatite (HAp), would trigger polymerization of model adhesives based on a popular self-etch monomer, 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP). The effect of 4E and HAp contents on degree of conversion (DC), polymerization rate (Rp), and induction period (IP) was investigated. The occurrence of such self-cure phenomenon in adhesives that underwent prior inadequate light cure was also evaluated. Model self-etch adhesives were prepared by using a monomer mixture of 10-MDP with 2-hydroxyethyl methacrylate at 1:1 wt. ratio. 4E (0.3–1.3 wt%), and HAp (0.5–2 wt%) were added to the mixture. Benzoylperoxide and N,N-dihydroxyethyl-p-toluidine were used as conventional chemical-cure system, and trimethylbenzoyl-diphenylphosphine oxide as light-curing photoinitiator. The polymerization processes and mechanical properties of model adhesives were evaluated by real time ATR/FT-IR and nanoindentation, respectively. The 4E- HAp system successfully triggered self-cure of 10-MDP based model adhesives. DC, Rp and IP were apparently affected by both 4E and HAp contents. DC of self-cure of the model adhesives was much higher than that of the conventional chemical-cure system. 4E-HAp initiated self-cure further boosted DC to ~100% regardless of prior light exposure, and significantly improved elastic modulus and hardness, thus provided a novel polymerization method to effectively salvage curing of the adhesives after inadequate light-cure.

Keywords

Self-etch adhesive; 10-MDP; tertiary amine; hydroxyapatite; self-cure; dual-cure

1. Introduction

Currently, acrylate-based resins dominate the chemical formulation of dental adhesives and composites [1–3]. Photo-initiated polymerization (light-cure) is the most favorable curing

method for dental resins mainly because of easy control on the onset of polymerization [4–7]. If light source is hampered in some circumstances, resin curing often suffers from poor polymerization, which leads to remaining of unreacted monomers and as a result, causes severe issues such as low bond strength, microleakage, cytotoxicity, and postoperative sensitivity [8–11]. In this situation, chemical-cure initiated by redox methods could be an alternative solution. It is common that both photo-initiators and chemical-cure initiators are added into the formulations of resin based materials [12–14]. This 'dual-cure' setting could improve polymerization and consequently led to a higher degree of conversion, especially in the areas where the light source was hard to reach [15–17]. Currently, the most popular chemical-cure system is two-component redox system consisted of benzoylperoxide (BPO) and a tertiary amine [18, 19]. However, this system features some critical drawbacks. Examples are inconvenient operational steps (admixture of two portions, limited time frame for adhesive application before polymerization, etc.), low storage stability caused by instability of BPO to light and heat[20], hydrolysis of BPO in aqueous system, and deactivation of the amine co-initiator in the presence of acidic species, which limit its application in water-containing adhesives, especially in self-etch adhesives containing acidic monomers.

Previously we reported a very unique spontaneous polymerization phenomenon of bis [2-(methacryloyloxy)ethyl] phosphate (2MP) mediated by ethyl 4-(dimethylamino)benzoate (4E) and hydroxyapatite (HAp) [21, 22]. This new initiation system induced self-cure of 2MP monomer at low pH and could be a good solution to dual-cure of acidic self-etch adhesives [23]. However, although the two phosphate groups of 2MP could offer strong capability of etching, there have been few studies reporting the application of 2MP as a self-etching monomer. 2MP has not been used in any of commercially available self-etch adhesives. The reason is probably due to its low Pka [24], leading to 'strong' self-etch, which induces rather deep demineralization effect on dentin, thus weakening the interfacial integrity [25]. In comparison, 10- methacryloyloxydecyl dihydrogen phosphate (10-MDP) has a mild etching capability indicated by its higher Pka [24]. Moreover, it has been found that 10-MDP could effectively form strong chemical bond to calcium of HAp, offering benefits in bond strength between the adhesive and tooth tissues [26]. The superior performance of 10-MDP has made it one of the most popular monomers in self-etch adhesives. According to previous studies, [21, 22] the interaction between acidic monomer 2MP and tertiary amine 4E, concentration of both 4E and HAp, and the acidity of the self-etch adhesive played critical roles in the occurrence of this kind of self-cure. Thus, it is totally unknown if self-cure of other acidic monomers, especially those used in commercial self-etch adhesives, would happen using this 4E-HAp system. Hence, it is of great clinical value to investigate if the mild acidic monomer 10-MDP is compatible with the 4E-HAp system to trigger its self-polymerization.

Thus, the aim of this study was to investigate the effects of 4E-HAp system and their contents on self-cure of 10-MDP based model adhesives, in comparison with the conventional chemical-cure system, and to investigate if such self-cure takes place in adhesives that underwent inadequate light cure in a dual-cure mode. The null hypothesis was that 4E-HAp system could not initiate the self-curing of the 10-MDP based adhesives under either situation.

2.   Materials and Methods:

2.1.   Reagents and abbreviations:

10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) was donated by Dr Huaibing Liu at Dentsply Sirona. 2-hydroxyethyl methacrylate (HEMA), ethyl 4-(dimethylamino)benzoate (4E), hydroxyapatite (HAp), benzoylperoxide (BPO), N,N-dihydroxyethyl-p-toluidine (DHEPT), and trimethylbenzoyl-diphenylphosphine oxide (TPO) were purchased from Sigma-Aldrich (Milwaukee, WI). Deuterium oxide (D_2O) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA).

2.2.   Model adhesive preparation:

Neat resin was prepared by mixing 10-MDP with HEMA at 1:1 weight ratio. 10-MDP was used as an acidic monomer and HEMA as a diluent monomer to decrease viscosity and increase hydrophilicity of the mixture. Then different initiators/components (except for DHEPT or HAp) were first dissolved in the monomer mixture, followed by adding of 20% (wt.) deuterium oxide (D_2O) to finalize the formulations (Table 1). Deuterium oxide was used instead of water because of its little interference to infrared spectra. Table 1 shows the formulations of 10-DMP based adhesives containing various initiators and other components. DHEPT (1.3 % with respect to adhesive) or HAp (0.5–2 %) was individually added to the deuterated adhesives, vortexed for 1 min, right before any of following measurements. Through the acid-base reaction, as much as 2.0 % HAp powder could be dissolved to obtain a clear, colorless mixture.

The initial pH value of each adhesive was measured with a pH meter (Accumet Excel XL15, Fisher Scientific). For each DHEPT or HAp containing adhesive, pH value was measured immediately after DHEPT or HAp incorporation. The pH meter was calibrated with three standard buffer solutions with pH values of 2.00, 4.00, and 7.00, respectively.

2.3.   Real-time ATR/FT-IR:

The polymerization processes of model self-etch adhesives were monitored by using a Fourier transformed infrared spectrometer equipped with an attenuated total reflectance (ATR) attachment (Spectrum One, PerkinElmer, Waltham, MA, USA). Each DHEPT or HAp- containing adhesive was vortexed for 1 min to facilitate DHEPT/HAp dissolution, and then one drop of adhesive was placed on the ATR top-plate, subsequently covered by a plastic cover slip. Programmed collection of spectra started instantly using TimeBase software (Perkin-Elmer). Continuous spectral collection was carried-out with up to 0.4- to 0.6-s spectral collection intervals depending on collection speed. For the light-cure only and dual-cure groups, after collecting the initial ~50 spectra, light irradiation began and lasted for 10, or 30 s. Conventional dental light (Spectrum Light; Dentsply, Milford, DE, USA) was used with output power at 600 mW/cm^2, and the curing tip was purposely set at a long distance (1 cm) away from the cover slip. Otherwise, all adhesive groups were shielded from the ambient light throughout spectral collection (up to 60 h). The spectra were recorded at a resolution of 4 cm^{-1} in the wave-number range between 700 and 4000 cm^{-1}. Due to high spectral quality, baseline correction was not needed.

2.4. Calculation of the degree of conversion (DC), polymerization rate (Rp), and induction period (IP):

Degree of conversion was calculated using the following equation:

$$DC = \left(1 - \frac{Absorbance^{cured}_{1637\ cm^{-1}}}{Absorbance^{cured}_{1455\ cm^{-1}}} \Big/ \frac{Absorbance^{uncured}_{1637\ cm^{-1}}}{Absorbance^{uncured}_{1455\ cm^{-1}}} \right) \times 100\%$$

The two-point baseline and maximum band-height ratio protocols were used to measure the absorption intensity. Rp was calculated with the maximum slope of the linear region of the DC versus time curve, simulated by least squares linear fitting. IP of the polymerization was determined as the time interval between the starting time point of the IR spectral collection and the point that DC of the adhesive significantly increased.

2.5. Nanoindentation:

The self-cure, dual-cure adhesives containing 4E (1.3 %) – HAp (2 %), and the light-cure only adhesive (Table 1) groups were subjected to nanoindentation tests. Specimens of the adhesives were fabricated in the sealed circular plastic molds (ID: 4.0 mm, Thickness: 0.4 mm) immediately after incorporation of 2 % HAp. Light-curing of both the light-cure and dual-cure groups was conducted with the conventional dental light for an exposure time of 20 s at a power output of 600 mW/cm^2 with 0.2 cm distance between the curing tip and cover slip to obtain solid resin discs. Specimens were then stored in dark for 24 h, demolded, well-polished and dried until the mass was constant. The tests were performed by using a nanoindenter (Triboscope, Hysitron Inc., Minneapolis, MN) attached to a Nanoscope IIIa atomic force microscope (AFM, Digital Instruments Inc., Santa Barbara, CA). A diamond-tipped indenter with an equilateral triangular base (Berkovich geometry) was calibrated before mechanical data collection. The indenter was applied at a loading/unloading rate of 200 μN/s and a load of 1000 μN, which were determined based on previous literature [27]. The nanoindentation data were acquired from at least 4 indentations in each of 3 specimens/group. The values of elastic modulus and hardness were obtained via the available Hysitron software.

2.6. Statistical analysis:

Statistical analysis of the experiments was performed via one-way analysis of variance (ANOVA), and comparisons of means were conducted via a Tukey's post-hoc test with a significance level of 0.05.

3. Results:

Representative time-resolved FTIR spectra in the wavenumber region of 1350–1800 cm^{-1} during self-cure of the model adhesive with the presence of 1.3% 4E and 2.0% HAp are shown in Fig. 1. As shown in the spectra, the model adhesive underwent self-cure starting at ~4 h and ending at ~10 h. The absorbance (or the height) of 1637 cm^{-1} band (C=C stretching) decreased, while that of 1455 cm^{-1} band (CH$_2$ scissoring), and 1715 cm^{-1} (C=O

stretching) remained almost unchanged in height as the polymerization proceeded. However, the 1715 cm^{-1} band shifted to higher wavenumbers when self-cure started. After 10 h, the absorbance band at 1637 cm^{-1} nearly vanished, indicating C=C bond was almost completely consumed. In other words, degree of conversion of the adhesive reached nearly 100% within 6 h.

Figure 2 shows the real-time DC plots and final DC, Rp and IP of the 10-MDP/HEMA model self-etch adhesives with the presence of 0.3–1.3% 4E and a fixed concentration of HAp (2.0%). Initiation of the adhesive with 0.3% 4E was slow, and the DC started to increase significantly after ~22 h. The increase stopped at about 40 h and the final DC was ~43%. By increasing 4E concentration, the self-cure was accelerated, indicated by increased Rp and reduced IP. Higher DC was also achieved with higher 4E content. After self-cure, ~100% DC was obtained for the groups with 1.0% or 1.3% 4E, indicating vinyl groups of monomers were almost completely consumed.

The effect of HAp concentration on self-cure of model adhesives was also studied (Figure 3). 0.5% HAp could trigger self-cure of the model adhesive, although the polymerization occurred after ~36 h with a very slow rate (Rp = 4.2%/h). After 60 h, over 75% of C=C group of the monomers was left unconsumed (DC=23%). Increasing HAp to 1.0% had a dramatic influence on IP, which was reduced from ~36 h to only ~5 h, with the Rp doubled and DC increased to 86%. For the groups with 1.5% and 2.0% HAp, most vinyl C=C groups of monomers were reacted, indicated by ~100% DC.

The DC vs time curves and final DC, Rp, IP of the 4E-HAp self-cure system and conventional chemical-cure system (BPO-DHEPT) are shown in Figure 4. Considering pH of the 4E-HAp group (pH~1.7) was higher than the BPO-DHEPT group (pH~1.0) due to the basicity of HAp, a third group with BPO-DHEPT and the same amount of HAp (pH~1.7) (in this case, 2% HAp was added right after incorporation of DHEPT) was also included for comparison. Chemical-cure of the BPO-DHEPT group took place quickly (IP=0.3 h); however, its polymerization rate was very slow (Rp = 2%/h), and the final DC (60 h) was only 19%, leaving over 80% C=C unreacted. For the BPO-DHEPT-HAp group, no polymerization was observed during 60 h. For the 4E-HAp group, self-cure occurred at ~1.8 h with a much higher Rp (56%/h) and final DC (~100%).

Effect of 4E-HAp in a dual-cure mode was studied by incorporation of both self-cure initiator (1.3% 4E, 2.0% HAp) and photo-initiator (0.6% TPO) into the 10-MDP/HEMA adhesive. The adhesive without 4E was used as the light-cure only group (Figure 5). In less than 10 min, DC stopped increasing and leveled off as a function of time. After 10 s or 30 s of light exposure, DC (DC$_0$) of the light-cure only group (without 4E) was 22% or 83%, respectively. During dark storage (20h), the DC remained no change, indicating no further polymerization occurred. However, for the dual-cure group (with 4E), apparent self-cure occurred at about 2 h and the DC was eventually increased to ~100% (DC$_{20h}$) regardless of initial DC$_0$ values.

DC and mechanical properties of the self-cure (4E+HAp), dual-cure (4E+HAp+TPO) adhesives in comparison with the light-cure only adhesive (TPO+HAp) are shown in Table

2. DC of the light-cure only group was 52%, leading to poor Er (0.03 Gpa) and hardness (2.82 Mpa). The dual-cure group showed significant better Er (3.25 Gpa) and hardness (226.92 Mpa), which were similar to the self-cure group's values (Er= 3.38 Gpa, Hardness= 241.50 Mpa). Both the dual-cure and self-cure specimens had DC of ~100%, consisted with the results of thin films in real time ATR/FT-IR tests (Figures 3 and 5).

4. Discussion:

The above results indicated that the 4E-HAp system indeed successfully triggered self-polymerization of mild acidic 10-MDP based adhesives in both self-cure and dual-cure mode (Figures 2, 3 and 5). Both 4E and HAp played a critical role in self-cure of the model adhesives. DC, Rp and IP were apparently affected by both 4E and HAp contents. Self-cure would not occur if the adhesives only contained either 4E or HAp (data not shown). The null hypothesis that 4E-HAp system could not initiate the self-curing of the 10-MDP based adhesives in a self- cure or dual-cure mode was rejected.

It is believed that the initiation mechanism is associated with the tertiary amine (4E) and acid (acidic monomer) complex, mediated by a base trigger (HAp). [21, 22] Radical polymerization initiated by amine-acid complex has been reported previously [28, 29] in dental bonding research. However, in these studies, the amines used are carboxyl-containing amines (e.g., N- phenylglycine, N-phenyliminodiacetic acid), which contain amine and acid on the same molecule. Since the amine-acid balance is constantly kept in the same molecule and a base trigger is not needed, these amines display the same weakness of conventional chemical initiation in terms of self/spontaneous polymerization. There is more acid (i.e., acidic monomer 10-MDP) than amine (4E) in our system, thus it requires additional base (HAp) to trigger the polymerization, resulting in user-controlled self-cure.

Concentrations of 4E and HAp showed great influence on self-cure of the model adhesive. As shown in Figure 2, by adjusting 4E content, IP and Rp could be controlled. 4E was effective enough in self-cure of the 10-MDP/HEMA adhesive at a relatively low concentration (0.3%), although polymerization was slow and more than half of the monomers did not polymerize during the tested time-frame. When the concentration of 4E was within the range of 1.0%~ 1.3%, nearly all monomers (~100%) polymerized within several hours. On the other hand, higher HAp content facilitated self-cure of the 10-MDP/ HEMA adhesive (Figure 3). 10-MDP/HEMA has mild acidity with capability to dissolve ~2.0% HAp, and undergoes relatively slow self- polymerization (IP=1.8 h, Rp=56%/h) with high final DC (~100%), which actually might be suitable for the potential strategy of self polymerization triggered by HAp directly from tooth mineral.

Figure 4 revealed that 4E-HAp was more effective than conventional BPO-DHEPT chemical cure system in polymerization of model 10-MDP/HEMA self-etch adhesive. In the presence of acidic monomer 10-MDP, the BPO-DHEPT group had very low Rp with over 80% unreacted monomers during tested time frame (60 h), while the 4E-HAp self-cure group achieved very high DC (~100%) within several hours. With the presence of 2.0% HAp, BPO- DHEPT even did not initiate polymerization, which was possibly due to faster hydrolysis of BPO at higher pH. In the 10-MDP based adhesive, besides the unique user-

controlled self-cure nature, the 4E-HAp system showed additional advantages over conventional BPO-DHEPT system in terms of polymerization effectiveness such as higher DC and Rp.

Although light-cure is the major curing method in dental adhesives, it shows limitations in some clinical situations where light-irradiation is hampered. When applied in a dual-cure mode, self-cure triggered by 4E-HAp successfully salvaged curing of the adhesive which underwent inadequate light-cure. Compared with the light-cure only group, the dual-cure groups benefited from self-cure shortly after light-cure (Figure 5). When comparing the two dual-cure groups, it seemed that IP and final DC of the self-cure phase were not affected by initial light-cure DC_0 (25% or 85%), while lower Rp (13%/h) was observed in the group with higher light-cure DC_0 (85%), which possibly due to higher viscosity and lower monomer concentration. In both inadequate light irradiation situations (long 1 cm distance between the curing tip and sample for 10 s and 30 s, respectively), 4E-HAp worked perfectly as a secondary initiation system. The mechanical characterization further confirmed salvaging of curing (Table 2). Under inadequate light exposure condition, light-cure adhesive showed low modulus (0.03 Gpa) and hardness (2.82 Mpa). By incorporation of self-cure (4E-HAp) function, huge improvement of modulus (3.25 Gpa) and hardness (226.92 Mpa) was achieved, consistent with the increased DC.

In general, the 4E-HAp system offers a very fascinating user-controlled self-cure method and several unique features. For example, there is abundant HAp in tooth enamel and dentin, [30] which makes it possible to trigger self-polymerization by simply applying the acidic 10-MDP containing primer/adhesive to tooth surface and obtaining adequate HAp through self-etching and 10-MDP-calcium interactions [25, 31]. In addition, currently, camphorquinone (CQ) is the most used photoinitiator for dental resins[6, 32]; and ethyl-4-dimethylaminobenzoate (4E), also termed as EDMAB/DMAB/EDAB in some literatures, is an effective co-initiator of CQ widely used in many commercial dental adhesives[33–35]. Considering minimum 4E concentration (0.3%) needed for self-cure and usual 4E concentration (1%) in commercial adhesives, we may have already taken advantage of the 4E-HAp self-cure feature but possibly not to the greatest level due to the lack of knowledge about it. 10-MDP is considered as the most promising monomer for chemical bonding to HAp of enamel or dentin [26]. Strong interaction between 10- MDP and HAp was believed to be responsible for enhanced bonding strength[26]. Based on this study, increased DC by 4E-HAp self-cure at the interface might also have played some role in bonding. Another unique feature is that the self-cure system could possibly make a good use of the unconsumed 4E after light-cure, thus there will be less concern about the cytotoxic risk induced by the amine, which is usually a concern in current adhesive systems.

In this proof-of-concept study, TPO was used as the photo-initiator as opposed to the widely used CQ/4E photo-initiators since the use of CQ/4E would disguise the role of 4E as a light-cure co-initiator and self-cure initiator. TPO, widely used in many light-curing resins [36–41], could initiate light-cure as quickly as the CQ system [42, 43] but without the involvement of 4E, which allows clear observation of 4E's role as a self-cure initiator. In addition, TPO's light- cure phase was short enough (<10 min) to permit obvious scrutiny of occurrence of self-cure phase without overlapping with the light-cure phase (Figure 5). For

the same reason, the simplified model adhesive formulation (10-MDP/HEMA) was used as the first step for this proof-of-concept study. Studies on the adhesive formulation containing CQ/4E and crosslinking monomers such as BisGMA are ongoing. Additionally, future work will be focused on in-situ 'smart self curing' of 10-MDP/4E based self-etch adhesives on tooth surface triggered by HAp directly from the tooth via etching other than inclusion of HAp in adhesives, as well as the influence of 10-MDP-calcium complexes in the interface on self-cure.

5. Conclusion:

In summary, we verified self-cure triggered by 4E-HAp could occur in the 10-MDP based self-etch adhesives in the presence of small amounts of 4E and HAp. 4E-HAp system might be a facile solution as a dual-cure system that offers additional benefits to curing of self-etch adhesives at the interface. Especially, as the main mineral component of enamel and dentin, HAp is highly available upon demineralization by self-etch adhesives. This offers considerable possibility to strengthen the bonding of adhesives through the observed self-cure when practically applied onto dentin or enamel substrates. It will be interesting to see if capability of 10-MDP to chemically bond with calcium could help with etching and delivering adequate HAp from demineralization to the adhesive in order to formulate a smart 'HAp-free' self-etch adhesive for *in situ* self-cure.

Acknowledgement:

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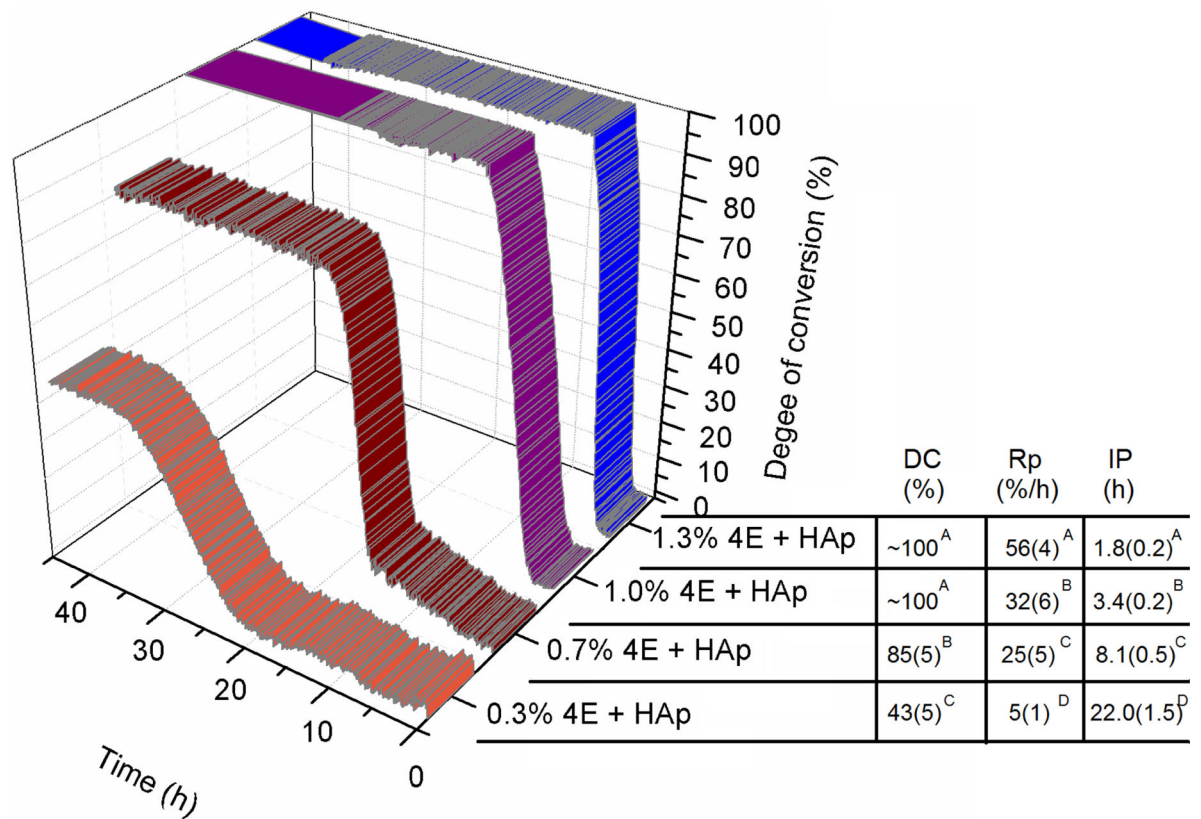
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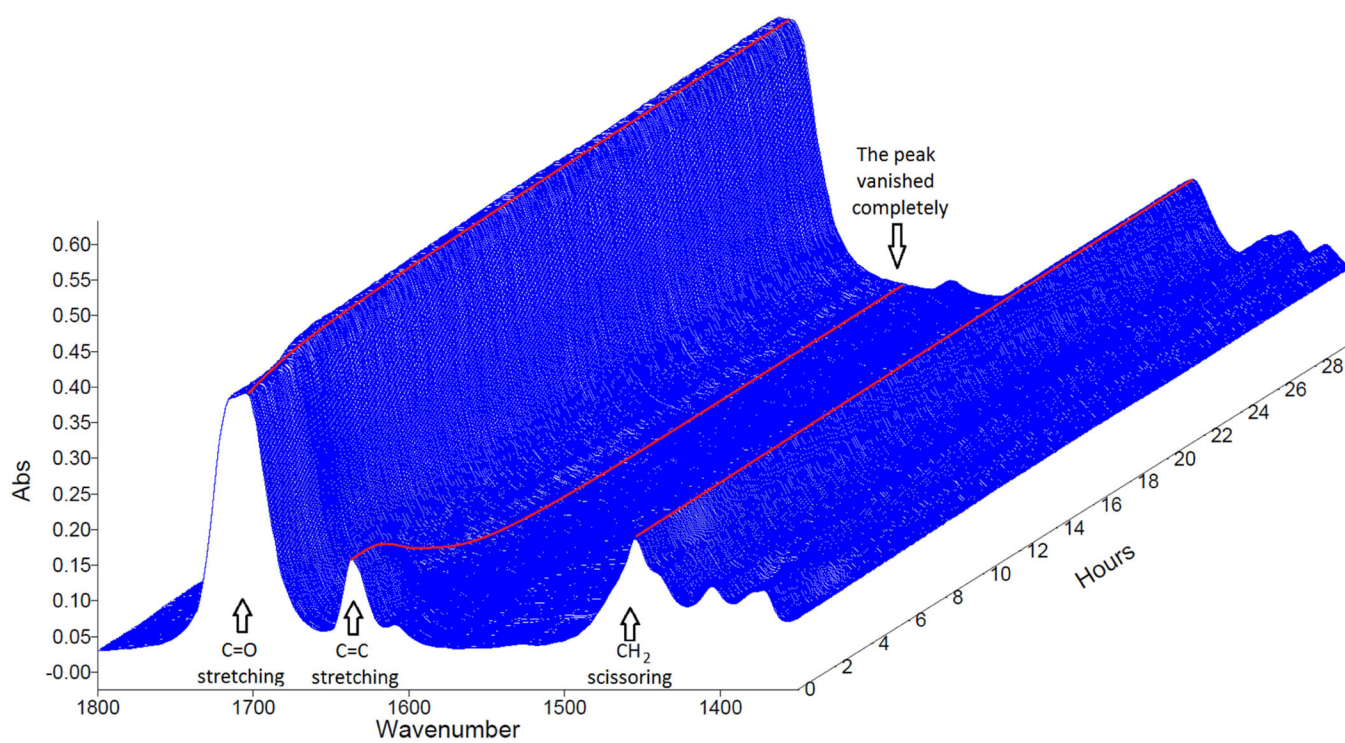
Figure 1.
Representative FT-IR spectra of the 10-MDP/HEMA model adhesive (1.3% 4E, 2.0% HAp)
during self-cure.

	DC (%)	Rp (%/h)	IP (h)
1.3% 4E + HAp	~100[A]	56(4)[A]	1.8(0.2)[A]
1.0% 4E + HAp	~100[A]	32(6)[B]	3.4(0.2)[B]
0.7% 4E + HAp	85(5)[B]	25(5)[C]	8.1(0.5)[C]
0.3% 4E + HAp	43(5)[C]	5(1)[D]	22.0(1.5)[D]

Figure 2.
Real time DC curves of model adhesives containing 4E-HAp self-cure system at a fixed HAp concentration (2.0 %) and variable 4E concentrations (0.3%, 0.7%, 1.0%, and 1.3%); DC (maximum), Rp and IP were summarized in means (S.D.) (n = 3), significant differences are indicated by distinct uppercase letters in the same column.

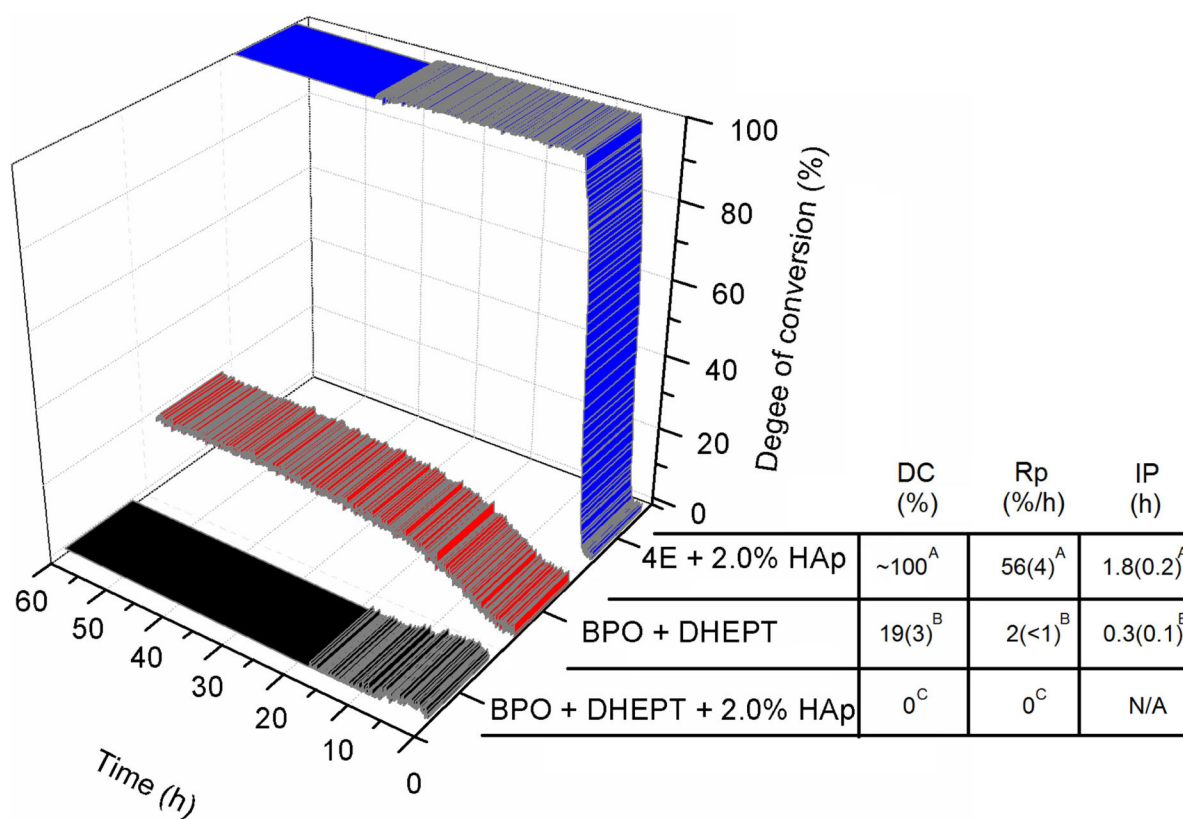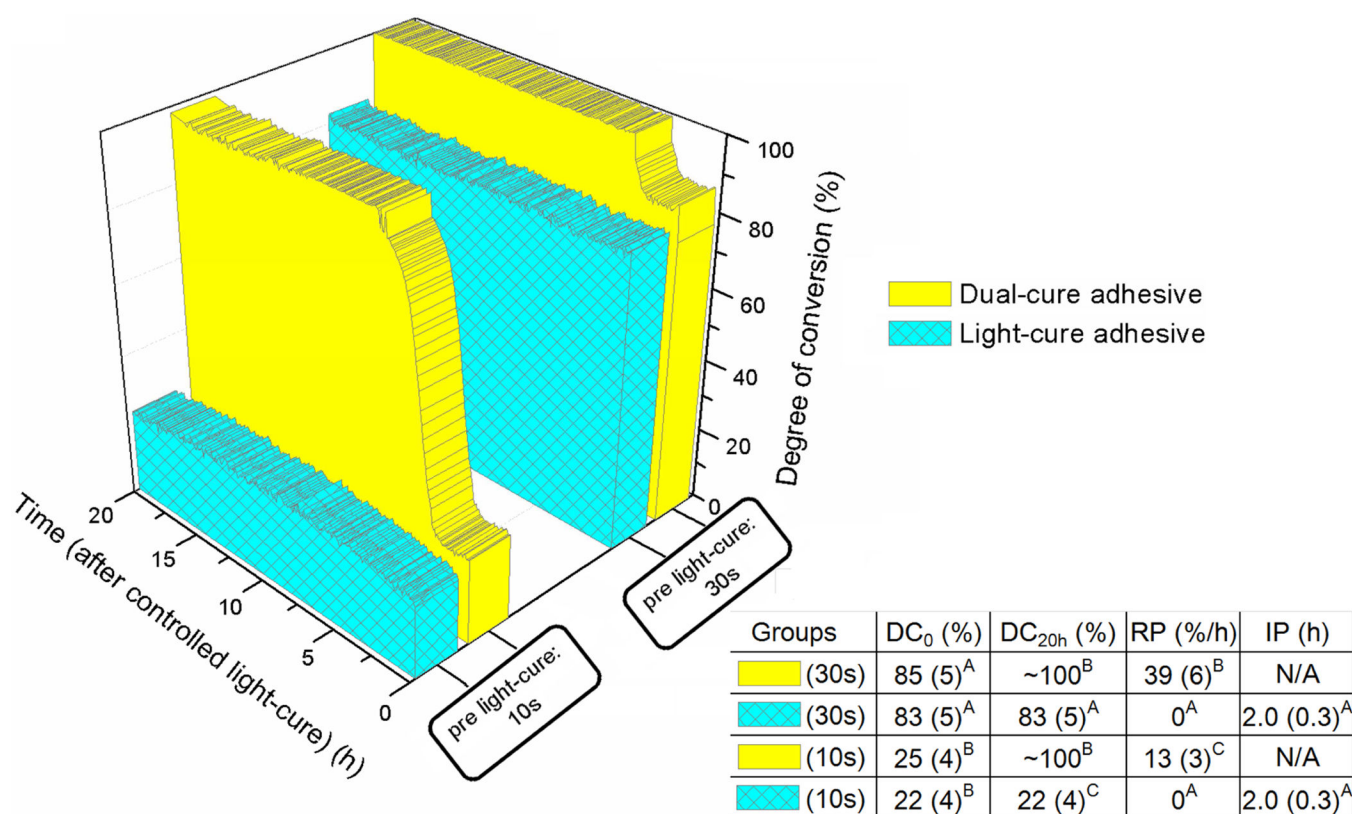|	DC (%)	Rp (%/h)	IP (h)
4E + 2.0% HAp	~100[A]	56(4)[A]	1.8(0.2)[A]
4E + 1.5% HAp	~100[A]	31(4)[B]	3.0(0.3)[B]
4E + 1.0% HAp	86(4)[B]	9(2)[C]	5.0(0.5)[C]
4E + 0.5% HAp	23(4)[C]	4(1)[D]	36.1(2.6)[D]
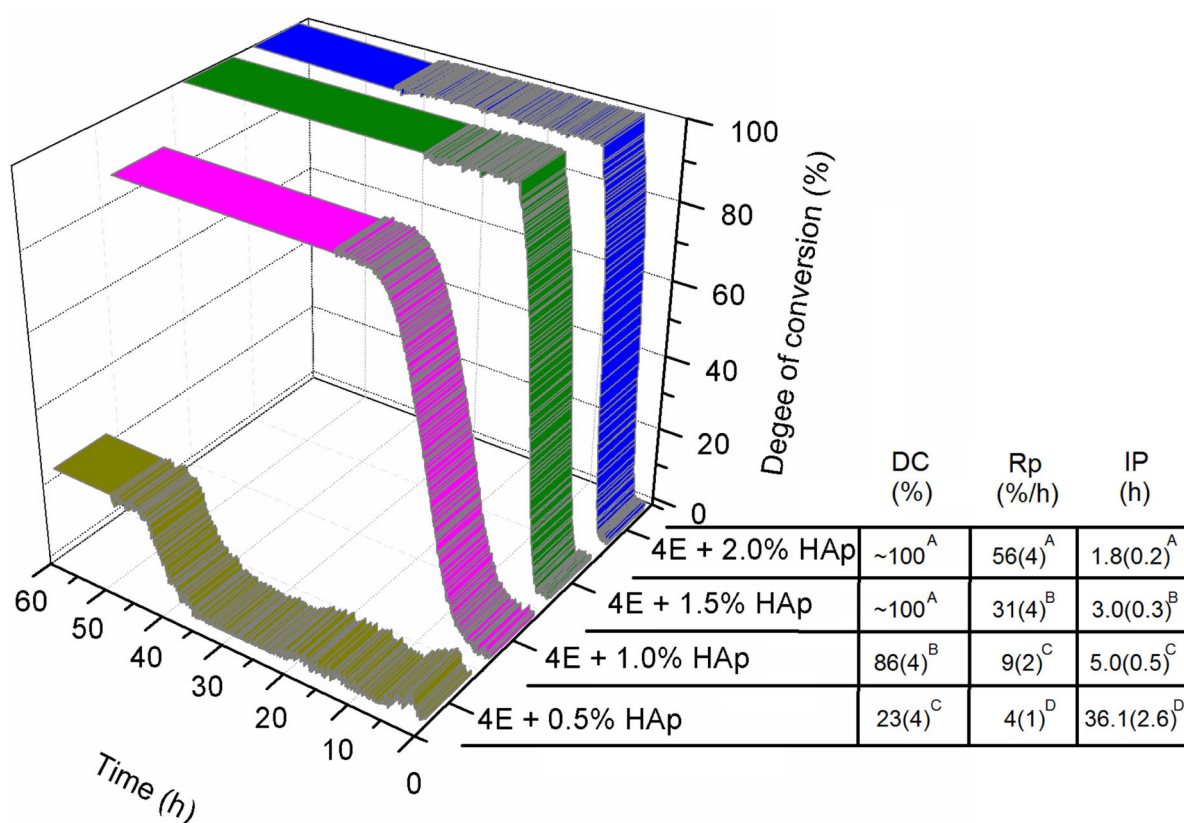
Figure 3.
Real time DC curves of model adhesives containing 4E-HAp self-cure system at a fixed 4E concentration (1.3 %) and variable HAp concentrations (0.5%, 1.0%, 1.5%, and 2.0%); DC (maximum), Rp and IP were summarized in means (S.D.) (n = 3), significant differences are indicated by distinct uppercase letters in the same column.

	DC (%)	Rp (%/h)	IP (h)
4E + 2.0% HAp	~100^A	56(4)^A	1.8(0.2)^A
BPO + DHEPT	19(3)^B	2(<1)^B	0.3(0.1)^B
BPO + DHEPT + 2.0% HAp	0^C	0^C	N/A

Figure 4.
Real time DC curves of model adhesives containing 4E-HAp self-cure system (4E + HAp) or conventional chemical-cure systems (BPO + DHEPT and BPO + DHEPT + HAp); DC (maximum), Rp and IP were summarized in means (S.D.) (n = 3), significant differences are indicated by distinct uppercase letters in the same column.

Groups		DC$_0$ (%)	DC$_{20h}$ (%)	RP (%/h)	IP (h)
▢	(30s)	85 (5)^A	~100^B	39 (6)^B	N/A
▨	(30s)	83 (5)^A	83 (5)^A	0^A	2.0 (0.3)^A
▢	(10s)	25 (4)^B	~100^B	13 (3)^C	N/A
▨	(10s)	22 (4)^B	22 (4)^C	0^A	2.0 (0.3)^A

Figure 5.
Real time DC curves of the light-cure only adhesive (TPO + HAp) and the dual-cure adhesive (TPO + 4E + HAp) during dark storage after 10 s, 30 s of light exposure; DC (0h, 20h), Rp and IP were summarized in means (S.D.) (n = 3), significant differences are indicated by distinct uppercase letters in the same column.

Table 1.

10-MDP-based adhesives used in this study.

Adhesive Groups used	Formulation of the adhesives (wt %)				
	Monomers		**Other components**		
	10-MDP+HEMA (1:1 wt)	**BPO**	**DHEPT**	**HAp**	**D₂O**
Conventional chemical-cure	78.3	0.8	1.3	\	19.6
	76.7	0.8	1.3	2.0	19.2
	10-MDP+HEMA (1:1 wt)		**4E**	**HAp**	**D₂O**
	78.6		1.3	0.5	19.6
	78.2		1.3	1.0	19.5
	77.8		1.3	1.5	19.4
Self-cure	77.4		1.3	2.0	19.3
	77.6		1.0	2.0	19.4
	77.8		0.7	2.0	19.5
	78.1		0.3	2.0	19.6
	10-MDP+HEMA (1:1 wt)	**TPO**	**4E**	**HAp**	**D₂O**
Dual-cure	76.9	0.6	1.3	2.0	19.2
Light-cure only	77.9	0.6	\	2.0	19.5

Table 2.

DC, elastic modulus and hardness of the light-cure only and dual-cure groups undergoing inadequate light exposure and 24h dark storage as compared with the self-cure group

Groups	DC (%)	Elastic modulus (GPa)	Hardness (MPa)
Light-cure only adhesive	52 (1)[A]	0.03 (0.01)[A]	2.82 (0.79)[A]
Dual-cure adhesive	~100[B]	3.25 (0.64)[B]	226.92 (68.69)[B]
Self-cure adhesive	~100[B]	3.38 (0.40)[B]	241.50 (51.49)[B]

Values were summarized in means (S.D.), (n = 3) significant differences are indicated by distinct uppercase letters in the same column.