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Effect of a non-thermal, atmospheric-pressure, plasma brush on conversion of model self-etch adhesive formulations compared to conventional photo-polymerization

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Abstract

Objective—To determine the effectiveness and efficiency of non-thermal, atmospheric plasmas for inducing polymerization of model dental self-etch adhesives.

Methods—The monomer mixtures used were bis-[2-(methacryloyloxy)ethyl] phosphate (2MP) and 2-hydroxyethyl methacrylate (HEMA), with mass ratios of 70/30, 50/50 and 30/70. Water was added to the above formulations: 10–30 wt%. These monomer/water mixtures were treated steadily for 40 s under a non-thermal atmospheric plasma brush working at temperatures from 32° to 35°C. For comparison, photo-initiators were added to the above formulations for photo-polymerization studies, which were light-cured for 40 s. The degree of conversion (DC) of both the plasma- and light-cured samples was measured using FTIR spectroscopy with an attenuated total reflectance attachment.

Results—The non-thermal plasma brush was effective in inducing polymerization of the model self-etch adhesives. The presence of water did not negatively affect the DC of plasma-cured samples. Indeed, DC values slightly increased, with increasing water content in adhesives: from 58.3% to 68.7% when the water content increased from 10% to 30% in the adhesives with a 50/50 (2MP/HEMA) mass ratio. Conversion values of the plasma-cured groups were higher than those of light-cured samples with the same mass ratio and water content. Spectral differences between the plasma- and light-cured groups indicate subtle structural distinctions in the resultant polymer networks.

Significance—This research is the first to demonstrate that the non-thermal plasma brush induces polymerization of model adhesives under clinical settings by direct/indirect energy transfer. This device shows promise for polymerization of dental composite restorations having enhanced properties and performance.

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Keywords

non-thermal plasmas; plasma-induced polymerization; self-etch adhesives; FTIR

1. Introduction

As a critical factor in improving the performance of dental composites, adhesive dentistry has greatly advanced, since Dr. Michael Buonocore [1] introduced the acid-etching technique. Clearfil Bond System-F (Kuraray Co., Ltd., Tokyo, Japan) was the first commercially available etch-and-rinse system, introduced in 1978, which was applied using “dry bonding”. In 1992 [2], the concept of “wet-bonding” to a dentin surface was introduced. This technique avoids collagen collapse due to over-drying of demineralized dentin [2,3], but the protocol is extremely sensitive to moisture and clinical handling. Additionally, excessive water on the dentin surface may dilute hydrophilic monomers [4,5], which results in phase separation, poor degree of double-bond conversion, and lower bond strength. In order to simplify the protocols and reduce technique sensitivity, acidic monomers are employed as self-etch adhesives.

The self-etch adhesive systems including one-step and two-step are believed to be more user-friendly and less technique-sensitive [6–8], and demonstrate lower incidence of postoperative sensitivity, compared to the etch-and-rinse systems [9]. However, some critical limitations still remain with self-etch adhesives, such as lower “immediate” bond strengths [10], increased interfacial nanoleakage [11, 12], enhanced osmosis and phase-separation in HEMA-rich formulations [13, 14], and continued demineralization of the surrounding hard tissue [15]. One of inherent problems [16] with these light-cured, self-etch adhesives is the compromised polymerization initiating efficacy, which arises from the reaction of acidic monomers with amines used in the initiator systems (such as the camphorquinone/amine system in the most of current adhesives) [16,17]. In addition, the presence of water dramatically decreases the degree of conversion and polymerization rate [17]. The combination of compromised photopolymerization, presence of water, and the hydrophilic nature of self-etch adhesives would likely contribute to the above mentioned limitations.

Plasmas are partially ionized gases that contain highly reactive particles including electronically excited atoms, molecules, ionic and free radical species. Depending on their gas temperature range (300–10,000 K) [18], plasmas can be divided into thermal (high temperature) and non-thermal (low temperature or cold) categories. Non-thermal gas plasmas also contain the above reactive particles, while the gas phase remains near room temperature. Applications of thermal and non-thermal plasmas include: surface etching and cleaning, surface engineering and functionalization, deposition of organic and inorganic functional coatings, and sterilization of solid state biomaterials and medical devices [19–23]. In dentistry, application of non-thermal plasma use has focused on killing of oral bacteria [24–27], dentin adhesion enhancement [28], and tooth bleaching [29].

It is also well known that plasmas induce polymerization [30–32]. Polymers synthesized by plasma exposure demonstrate high cross-linking and high degrees of polymerization [33–35]. However, plasmas used for these applications are created under a low pressure, high vacuum environment, which is not applicable to *in vivo* conditions. The need of reduced pressure or high vacuum for generating plasmas limits its biomedical applications. Plasmas created at one atmospheric pressure are usually of the high temperature nature, due to high gas density. Such high temperatures cannot be endured by living organisms, especially in the oral cavity. For example, the dental pulp is a very sensitive tissue: an intrapulpal

temperature increase of 5.5°C will result in 15% of pulp tissue necrosis [36]. Recent development in atmospheric plasma technology has enabled generation of plasmas at a relatively low temperature. The patented nonthermal atmospheric plasma brush, developed in our plasma research center, can be ignited and sustained in an ambient atmosphere, at very low power consumption (several watts), with temperatures close to that of the human body. Previous studies indicate that this brush was highly effective in oral bacterial disinfection and interfacial bonding improvement of composite restorations.

Thus, the purpose of the current study is to examine the effectiveness of the non-thermal, atmospheric-pressure, plasma brush for inducing polymerization of one-step, model self-etch adhesives, without inclusion of photoinitiators. Conventional photo-activated polymerization of the model resin system was used as control. The research hypothesis tested was that the extent of monomer conversion of the model resin system would be significantly greater when using the plasma brush than when the same system was conventionally light-cured. In addition, it was hypothesized that the presence of water would not have a significant impact on resin conversion when using the plasma brush, but would cause a significant decrease in conversion in the photo-initiated systems.

2. Materials and methods

2.1 Model self-etch adhesive preparation

The monomer mixtures used in this study consisted of bis-[2-(methacryloyloxy)ethyl] phosphate (2MP) (Sigma-Aldrich, Milwaukee, WI, USA) and 2-hydroxyethyl methacrylate (HEMA) (Acros Organics, Morris Plain, NJ, USA). Resins were mixed in a mass ratio (2MP:HEMA) of 30:70, 50:50, 70:30, respectively. The chemical composition of the model resin system is similar to that of a commercial, self-etch adhesive (Clearfil Liner Bond 2V, Kuraray America, Inc., New York, NY, USA, based on the MSDS sheet). For comparison, photoinitiators, such as camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDMAB), were added to above formulations to provide photo-activation capability. Photoinitiator concentration (for each component) was maintained at 0.022 mmol per gram of the monomer mixture, according to previous results [17]. The photo-initiators were all obtained from Sigma-Aldrich and used without any further purification.

Deuterium oxide (D₂O, Cambridge Isotope Laboratories, Inc., Andover, MA), at concentrations of 10, 20, or 30 wt %, was used to make the self-etch adhesive solutions. Using D₂O instead of H₂O avoided the interference in the IR absorption of H₂O with that of C=C double bonds in adhesives. Sufficient shaking and sonication were required to yield well-mixed solutions.

2.2 Non-thermal, atmospheric plasma brush

The non-thermal, atmospheric plasma brush employed in this study was designed by the Plasma Research Center at University of Missouri and Los Alamos National Laboratory. The detailed information about this device can be found in previous publications [37, 38]. Compressed argon gas (ultra high purity) was used as the plasma gas supply. A mass flow controller (MKS Instruments Inc., Andover, MA) was introduced to adjust the argon gas flow rate. A glow discharge by the direct current power source (Model 1556C, Power designs Inc, Westbury, NY) was ignited between the two electrodes in a Teflon chamber. Figure 1 shows a photograph of the plasma brush in the atmospheric environment. Plasma temperatures were characterized by a type K thermocouple and infrared imaging (TH 5104, Mikron Infrared Inc, Oakland, NJ).

2.3 FTIR spectroscopy

The infrared (IR) spectra of monomers, plasma-cured and light-cured adhesives were obtained using a Fourier transform infrared spectrometer (Spectrum One, Perkin-Elmer, Waltham, MA, USA) equipped with a universal attenuated total reflectance (ATR) attachment (Perkin-Elmer) at a resolution of 4 cm^{-1} . 128 scans were used and averaged to obtain a single spectrum. The ATR crystal was diamond with a transmission range between 650 and 4000 cm^{-1} .

2.3.1 Spectra of model adhesives before curing—A small volume of the adhesive/water mixture was cast on the diamond crystal top-plate of the ATR accessory, covered with a clear, polyester film (Mylar, $22 \times 22 \times 0.25\text{ mm}$, Fisher Scientific, Pittsburg, PA, USA). Spectra of the mixtures without any curing/treatment were obtained, and acted to supply absorption parameters of the specimens in the uncured state, which were used for calculation of the degree of conversion described below.

2.3.2 Spectra of plasma-cured adhesives—Glass slides were employed as the smooth solid substrates for the plasma-cured specimens. Each glass slide was uniformly treated with the non-thermal plasma brush for 60 s before applying one of photoinitiator-free model adhesives onto it, which made it possible for the adhesive to spread evenly on the surface. The adhesive/water mixtures were cast on the glass slides to form very thin liquid films, and were then treated/cured using the non-thermal, plasma brush for 40 s steadily (as schematically shown in Figure 2). The glass slides with plasma-cured adhesives were turned over and pressed against the horizontal face of the ATR diamond crystal where total internal reflection took place. The spectra of these plasma-cured adhesives were recorded. Six separate replications for each adhesive formulation were conducted.

2.3.3 Spectra of light-cured adhesives—The model adhesives containing photoinitiators were cast on the diamond crystal top-plate, covered with a clear, polyester film, and exposed for 40 s to a conventional dental light polymerization unit (Spectrum Light, Dentsply, Milford, DE, USA). The irradiance of the light (550 mW/cm^2) was measured using a visible curing light meter (CURE RITE, EFOS inc., Williamsville, NY, USA), having a digital display. The spectra of the light-cured adhesives were obtained. Three separate replications for each adhesive formulation were conducted.

2.4 Calculation of the degree of conversion

Two characteristic bands 1637 cm^{-1} (stretching of methacrylate double bond $\text{C}=\text{C}$) and 1715 cm^{-1} (stretching of carbonyl group $\text{C}=\text{O}$) were employed to calculate the DC of polymerization induced by both the light and non-thermal plasma curing. The intensities of these two bands were calculated based on band height methodology, and the changes of the band ratios profile at 1637 cm^{-1} and 1715 cm^{-1} were monitored. The DC was calculated by the following equation: [17]

$$DC = \left(1 - \frac{\text{Absorbance}_{1637\text{cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1715\text{cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1637\text{cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1715\text{cm}^{-1}}^{\text{monomer}}}\right) \times 100\% \quad (1)$$

Two-point baseline and maximum band height ratio protocol were used to measure the absorption intensity. Six (for plasma-cured system) or three (for light-cured system) spectra were employed to generate a mean DC value for each adhesive formulation.

2.5 Statistical analysis

DC values are represented as means $\pm$ standard deviation (SD). Two-way analyses of variance (ANOVA) were used to evaluate the interaction between curing mode (plasma or light) and D₂O content (3 levels). Where there was a significant interaction term, the differences between DCs (%) of light-cured and plasma-cured were evaluated by two-tailed Student's t-test, and the differences among 10, 20, and 30 wt% water (D₂O) contents and same curing mode were evaluated by one-way ANOVA with Tukey's post test. All statistical analyses were performed using GraphPad InStat, version 3.06, software (GraphPad Software, San Diego, CA, USA). Significance was noted at $p < 0.05$.

3. Results

Fig. 1 shows a photograph of the plasma brush in the atmospheric environment. The flame length and gas phase temperature of the plasma brush depended on argon flow rates and electric power inputs. When the argon flow rate was set at 3000 sccm and the input power was 5 Watts, the length of the brush was about 7 mm (Fig. 1). Under this condition, the temperatures of 32–35°C were measured on the adhesive surface (Fig. 1), which were close to the body temperature. Thus, these parameters (3000 sccm, 5 W) were chosen and kept unchanged throughout this study. Schematic illustration of the various free radicals and charged particles within the flame of the plasma brush is shown in Fig. 2.

Representative IR spectra in the region of 1800–1350 cm⁻¹ for the 2MP/HEMA=50/50 model adhesive with 20 wt% water, before and after light curing for 40 s, are shown in Figures 3a and 3b, respectively. A representative spectrum of the same monomer composition, but photoinitiator-free model adhesive containing 20 wt% water after plasma curing for 40 s is shown in Figure 3c. The absorption band occurring near 1715 cm⁻¹ is associated with carbonyl group, and the band at 1637 cm⁻¹ is associated with unpolymerized, methacrylate C=C in the adhesive monomers. In these spectra, the absorbance at 1637 cm⁻¹ decreased in both spectra of the model adhesive after either 40-s light- or plasma- exposure. The decrease in absorbance of this band indicates consumption of methacrylate C=C bonds during curing/polymerization. The absorption intensity (height) at 1637 cm⁻¹ in the spectrum of plasma-cured samples decreased more than that of light-cured samples after the same 40-s curing time.

The DCs of the model adhesives with different monomer mass ratios and different water contents were calculated based on Equation 1, and are shown in Fig. 4. Two-way ANOVA showed that there was significant interaction between curing mode and water content. Under all the tested conditions, the DCs (51.4–68.7%) of the plasma-cured samples were all higher than those (13.9–43.0%) of the light-cured ones ($P < 0.05$). It was interesting to notice that the DC increased with increasing water content in each of plasma-cured adhesive groups. For example, in the 2MP:HEMA=70/30 adhesive group, the DC increased from 51.4% to 61.5%; in the 50/50 group, from 58.3% to 68.7%; and in the 30/70 group, from 62.7% to 66.1%. The highest DC (68.7 $\pm$ 1.6%) was achieved for the 50/50 adhesive with a water content of 30%. For the DCs of the light-cured samples, the correlation of DC as a function of water content was totally opposite. With the increase of water content, the DC decreased dramatically in each of light-cured adhesive groups: it fell from 43.0% to 19.0% in the 2MP/HEMA=70/30 adhesive group, from 40.1% to 16.4% in the 50/50 group, and from 26.5% to 13.9% in the 30/70 group, respectively.

Representative IR spectra in the region of 3800–1350 cm⁻¹ for the 2MP/HEMA=50/50 model adhesive containing 20 wt% water after plasma- and light-curing were compared as shown in Figure 5. Besides the difference in C=C discussed above, there were noticeable differences in the -CH₂ and -CH₃ group region around 1400 cm⁻¹ and the band width/shift

of the carbonyl group around 1700 cm^{-1} (indicated by arrows). Inserted in Figure 5 is an enlarged view of the spectral region in the range of $2800\text{--}3800\text{ cm}^{-1}$. From the spectra, additional differences are evident within the following regions: the O-D group region of D_2O at $2300\text{--}2700\text{ cm}^{-1}$ (with the vibration frequency of maximum intensity at 2500 cm^{-1}), the $-\text{CH}_2$ and $-\text{CH}_3$ group region at $2800\text{--}3000\text{ cm}^{-1}$, and the $-\text{OH}$ group region at $3200\text{--}3600\text{ cm}^{-1}$ (with the vibration frequency of maximum intensity at 3420 cm^{-1}). In the spectrum of the plasma-cured group, the absorbance of the 2500 cm^{-1} ($-\text{OD}$) band decreased dramatically, while that of 3420 cm^{-1} ($-\text{OH}$) increased as compared to the spectrum of light-cured group.

4. Discussion

The two research hypotheses proposed in this study were accepted. The present FTIR results clearly indicate that the atmospheric, non-thermal plasma exposure induced polymerization of the photoinitiator-free self-etch adhesives. DC values of the plasma-cured groups were higher than those of light-cured groups with the same composition (Fig. 4). The presence of water did not negatively influence the DC of plasma-cured samples, but triggered a decline in DC of the light-cured samples (Fig 4). It is well known that plasmas can be used to initiate polymerization to produce high molecular weight polymers [31]. However, these plasmas are normally generated under low pressure and/or high vacuum. In this study, for the first time, it was proven that polymerization of dental adhesives could occur by using the plasma brush under ambient conditions.

The polymerization processes under a plasma environment generally include plasma-induced polymerization and plasma polymerization (so called “plasma-state polymerization”). The first item is not limited to liquid- or solid-phase reaction, and the later is limited to the plasma phase (i.e. the gas phase) and the interface in contact with plasmas. According to Yasuda [39], both polymerization processes likely took place in the adhesives. However, because of very low evaporation capability of the monomers used (for example, the vapor pressure of HEMA is 0.01 mm Hg at $25\text{ }^\circ\text{C}$), the occurrence of plasma-state polymerization is less possible and could be ignored [40]. Plasma-induced polymerization likely produced nearly all of the plasma-cured adhesive resins.

For an adhesive system using conventional curing methods, chemical- or photo-initiators are indispensable to provide the needed free radicals, to produce the essential initiation by adding onto the vinyl double bonds, and resulting in chain-growth polymerization. For an initiator-free adhesive exposed to plasmas, the energy from collisions of excited particles (direct transfer) and the irradiation of photons (indirect transfer) are transferred to the monomers [32, 41], which results in cleavage of vinyl double bonds, formation of di-radicals, and thus polymerization. Although both polymerization modes are involved with free-radical reactions, the mechanisms of these two methods are not the same. These reactions are shown below [31].

I: initiator(s); R: radical; M: monomer; M: di-radical; P: polymer; i, j: number of monomer units.

In the conventional adhesive system, free radicals are produced by initiators, and the production and consumption rates are similar to the chain termination rate. In the plasma-initiated system, the di-radicals formed by plasmas react with both monomers and other di-radicals. With the conversion from monomer to polymer, the viscosity of the reaction system increases rapidly, which leads to trapping of radicals in the end-product, due to the decrease of polymer chain mobility. These residual radicals are considered as macromolecular initiators, and are available to react with other materials in which they come into contact, such as composites to be added or even oxygen in air, which make plasma-cured surface very active.

The DCs of plasma-cured samples were constantly higher than those of light-cured ones with the same 2MP/HEMA ratio and water content (Figure 4). For example, the DC of plasma-cured samples was $68.4 \pm 1.3\%$, while the DC of light-cured ones was only $20.8 \pm 0.3\%$ for 2MP/HEMA=50/50, 20% D₂O. It has been reported that the presence of acidic monomers in the self-etch adhesives negatively influence the efficiency of photoinitiators [16]. The acidic monomers are thought to react with amines of the initiating system and reduce amine concentration. Thus, the amount of amine radicals formed that initiate the photo-polymerization is reduced. This influence contributed a great extent to the observed low levels of DC via light-curing. The intrinsic problem associated with photo-initiation of self-etch adhesives was not observed in the plasma-initiated system. The reactive species in plasmas were not affected by the monomer acidity, and thus generated higher DCs of cured adhesives.

Water plays a critical role in the performance of self-etch adhesives bonding to dentin. On one hand, the presence of water in self-etch adhesives is essential for ionization of acidic monomers. Self-etch adhesives generally contain a certain amount of water (10–20%). For example, the self-etch adhesive Adper Prompt L-Pop contains ~20% water in its formula [15]. On the other hand, water might be an interfering factor for photo-polymerization of the adhesives [4,15]. This inhibition can be verified from the data presented in Fig. 4. When the water content increased from 10% to 30%, the DCs of light-cured specimens decreased dramatically. This reduction might be due to the fact that the system was too dilute to supply adequate free radicals for photo-polymerization. Under *in vivo* conditions, there might be higher water content in the region of the adhesives, due to a continuous outflow of water from tubules. Therefore, 3–5 s air-drying is typically required after application of self-etch adhesives. However, only less than half of the water/solvent is removed using this process[42]. Over-wet and phase separation phenomena may occur under these wet bonding conditions [5], resulting in an inhomogeneous structure of the adhesive layer which might be a potential mechanism for degradation [43].

The effect of water on DC was totally different for the plasma-initiated system. The results presented in Figure 4 reveal that the DCs of plasma-cured adhesives showed much less dependence on water content. Moreover, the DCs even slightly increased with additional water content (Figure 4). Some potential reasons for this trend rely on the fact that the photoinitiator-free, plasma-cured system avoided the intrinsic problem associated with photo-initiation mentioned above. The presence of water and acidity of adhesives has no effect on the plasma-initiated system. Secondly, proper water concentration could reduce adhesive viscosity, increase mobility of plasma injected free radicals and monomer molecules, and enhance chain propagation. Conversion values of the adhesive groups containing 30% water were always higher than those containing 10% water (Figure 4). In addition, during continuous injection of reactive species into the adhesive using the plasma

brush, the water was also gradually removed by the argon air flow (Figure 5). All these results indicate that plasma-initiated polymerization eliminates the negative effects of water, which is very applicable under *in vivo* conditions.

The spectral differences between the plasma- and light-cured groups may also indicate some structural distinctions in the resultant resins. The -OH region between 3200–3600 cm^{-1} with the maximum intensity at 3420 cm^{-1} , is related to hydrogen bonding (H-bond). In the spectrum of plasma-cured group (Figure 5), the absorbance of this band increased as compared to that of light-cured group. The increase of this band intensity might be due to more -OH species produced by plasma treatment [44, 45]. As described above, free-radicals trapped in the plasma-cured adhesives may react with O_2 or H_2O in an ambient environment, forming new oxygen-containing groups and thus more H-bonds. These newly formed functional groups make the surface more active, which could result in better adhesion to composites. The absorption shoulder near 3250 cm^{-1} appeared in the spectra of plasma-cured samples (Figure 5) could also be assigned to H-bonding. The band near 3420 cm^{-1} is believed to be associated with intra-molecular H-bonding, and the band near 3250 cm^{-1} is associated with intermolecular H-bonding [46]. Since O-H stretching vibration of the H-bond usually shifts towards lower frequencies when the bond is strengthened [46], higher absorbance of intermolecular H-bonding at 3250 cm^{-1} may suggest that there is stronger interaction among molecular chains in plasma-cured samples than in light-cured ones. Another spectral difference lies in the $-\text{CH}_2$ (2930 cm^{-1}) and $-\text{CH}_3$ (2980 cm^{-1}) bands. The absorbance of the $-\text{CH}_2$ band in the spectra of plasma-cured samples was lower, and that of the $-\text{CH}_3$ band was higher than those observed for the light-cured spectra, which suggests that the plasma-cured adhesives might contain a higher degree of branching [39]. Furthermore, it is reported that the plasma-cured polymers usually have higher molecular weight [31], and exposure to plasmas always leads to surface crosslinking [47]. As a result, the plasma-induced structural changes may also improve the hydrolytic stability of the resulting resins. Previous studies show that the non-thermal, plasma brush is very effective in disinfection of oral bacteria and in improving adhesive/dentin interface bonding [27, 28]. This plasma brush could potentially become a promising technique in various dental composite restoration applications for improved performance.

5. Conclusion

Within the limitations imposed in the current study, the following conclusions may be made:

1. It was proved for the first time that the non-thermal, atmospheric-pressure, plasma brush could be used to induce polymerization of photoinitiator-free model adhesive system under clinical settings.
2. The degree of monomer conversion of the model adhesive system was significantly greater when using the plasma brush than when the same system was conventionally light-cured.
3. In addition, the presence of water did not have a significant impact on resin monomer conversion when using the plasma brush, but caused a significant decrease in conversion in the photo-initiated systems.
4. There were spectral differences between the plasma- and light-cured groups, indicating subtle structural distinctions in the resultant resin networks.

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Figure 1.

Photograph of the plasma brush in atmospheric environment (left) and IR image of the plasma temperatures (right). Plasma conditions were 3000 sccm argon, and 5 W direct current power input.

Figure 2.

Schematic illustration of the plasma brush being applied onto the model adhesives. Within the flame of the plasma brush, there are many reactive plasma species including various free radicals and charged particles.

Figure 3.

Representative FTIR spectra of the model adhesives, before (3a) and after light- (3b) or plasma-curing (3c). 2MP/HEMA = 50/50, D₂O = 20%. The absorption band occurring near 1715 cm^{-1} is associated with carbonyl group, and the band at 1637 cm^{-1} is associated with unpolymerized, methacrylate C=C in the adhesive monomers.

Figure 4.

Percent monomer degree of conversion (DC) values of the model adhesives having different monomer mass ratios and different water contents (wt%). The adhesives were either plasma-cured or light-cured for 40 s. Values are mean (error bar: standard deviation, $n = 3$ for the light-cured group, $n = 6$ for the plasma-cured group). In each figure (4a, 4b or 4c), means with different letters are significantly different ($P < 0.05$).

Figure 5.

Representative IR spectra in the region of 3800–1350 cm^{-1} for the 2MP/HEMA=50/50 model adhesive containing 20 wt% water after plasma- or light-curing. The wavenumbers noted by arrows and their associated assignments are as follows: 1637 cm^{-1} (unpolymerized, methacrylate C=C), 1715 cm^{-1} (carbonyl), 2500 cm^{-1} (-OD of D_2O), 3420 cm^{-1} (-OH, intra-molecular H-bonding); in the inserted figure, 2930 cm^{-1} (-CH₂), 2980 cm^{-1} (-CH₃), 3250 cm^{-1} (-OH, intermolecular H-bonding), 3420 cm^{-1} (-OH, intra-molecular H-bonding).