Original Article

Effect of Water on HEMA Conversion by FT-IR Spectroscopy

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Abstract:

Objective: The use of HEMA as a biocompatible material in dentin bonding systems and its potential for clinical applications has been well established. Excess water can affect conversion of bonding resins. The aim of this study was to survey the effect of water on the degree of conversion of HEMA by Fourier Transform Infra-red Spectroscopy (FT-IR).
Materials and Methods: In this experimental study, distilled water was added in amounts of 0, 0.05, 0.1, 0.2, and 0.4 ml to 1 ml of curable HEMA solution. Six repetitions per water ratio were made and investigated. Each sample was polymerized for 60 seconds. Degree of conversion was obtained from the absorbance IR-Spectrum of the materials before and after polymerization by FT-IR spectroscopy. One way ANOVA and Tukey-HSD were carried out to compare and detect any differences among groups.
Results: Statistical analysis indicates highly significant difference between pairs of groups at level ($P<0.001$). The results showed a trend of decreasing in HEMA conversion with increasing water. Degree of conversion changes significantly within the 0.05 ml to 0.2 ml water range. However, degree of conversion did not change after reaching 0.02 ml and before 0.05.
Conclusion: Degree of conversion of HEMA decreased by increasing water. The most dramatic effect of water on the polymerization process occurs within a range which exists under clinical conditions. The reason that the degree of conversion did not show significant result before 0.05 ml may be related to the hydrophilic nature of HEMA.

Key Words: HEMA; Degree of conversion; FT-IR spectroscopy

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INTRODUCTION

Dimethacrylate monomers undergo are responsible for extensive cross-linking on polymerization; however, considerable residual monomer may remain in the final product. This ranges 25-45%, which can lead to degree of conversion ranging from 55 to 75% [1-3].
The conversion of dental resins has been evaluated by the investigation of physical properties, such as hardness, wear resistance, tensile and compressive strength, etc. [1-12]. Infrared (IR) Spectroscopy has been used for the determination of monomer conversion in dental restorative resins [1,3,13].
2-hydroxyethylmethacrylate is a biomedical monomer. As a methacrylate derivative, it is easily polymerized and of great interest for dental use. HEMA is extensively used as an important component of bonding to acid-conditioned dentin. HEMA was first reported by Fusayama who reported this monomer may enhance bond formation to dentin [14]. Others

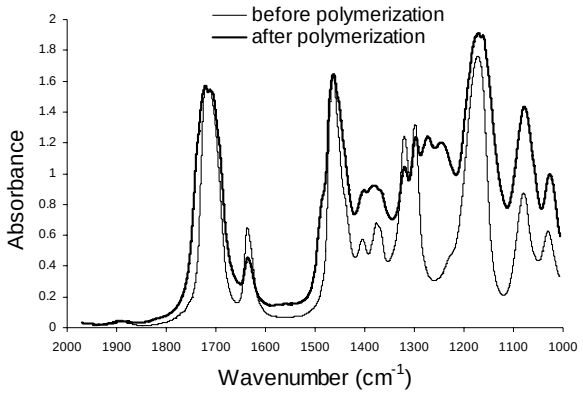

Fig 1. IR spectra of solution 1 (no water) before and after polymerization by 60s light curing.

reported that HEMA are responsible for the adhesion because of the diffusion properties of it [15-18]. HEMA along with other adhesive monomers, entangle matrix. It provides mechanically attaching restorative materials to dentin. Microscopic analysis of the bonding interface showed this mechanism [15-17,19-22].

Infiltration of the bonding agent together and polymerization, and also copolymerization with the HEMA molecules, may happen. Assuming that water may be retained in the HEMA and diffusion of the light activating components may be delayed by interference with the collagen fibers [23]. As a result of this, significant differences in the quality of the hybrid layer may happen. Such differences in quality may cause local stress concentrations. It will be capable of initiating bond failures for an adhesive joint. Insufficient polymerization of the bonding agent may cause a weak hybrid layer which decreases the bond strength. In addition, the presence of residual monomer can make degradation in the polymeric matrix. As a result, it is important to achieve a complete cure of bonding agent. As a result, inadequate polymerization inside of the hybrid layer may cause for monomer release. Thus it shows cytotoxic potential.

The aim of this study was to survey the effect of water on degree of conversion of HEMA by Fourier Transform Infra-Red (FTIR) Spectroscopy.

MATERIALS AND METHODS

A curable HEMA solution was made by mixing 98.7% (w/w) HEMA, 0.5% (w/w) CQ and 0.8% (w/w) DMPT (Table 1). Then, distilled water was added in amounts of 0.05, 0.10, 0.20, and 0.40 to 1ml of HEMA (Table 2). The vials were then immersed in an ultra-sound bath and mixed for 10 minutes. Six repetitions per water ratio were made and investigated. One drop of HEMA solution was placed on the middle of a clean polythene plate (thickness = 25.4 μm, and diameter = 26 mm). This drop was covered with another polythene plate. Diameter of the upper polythene film was 15 mm in order to obtain a seal and uniform sandwich of HEMA between two polythene plates. Then, the plates were placed in the sample holder, which was located outside the sample compartment of the FT-IR. This procedure was done before and after curing for each specimen. Their light outputs were tested by radiometer (model 100 Optilux radiometer, Danburg, CT 06810); which obtain over 800 mW/cm^2 for coltolux 75. Time of light curing was 60s.

Nicolet FT-IR (MAGNA-IR Spectrometer 750) was used to analyze the unreacted methacrylate groups. The specimens were placed in the sample compartment of the FTIR instrument, and the spectra were obtained using 10 scans at a resolution of 4 cm^{-1} and a wave number range of 2000-550cm^{-1}.

For calculating the degree of conversion (DC), the ratio of the absorbance intensities of C=C/C=O were compared before and after polymerization. Then, determination of the per-

Table 1. Materials used in this study.

Material	Lot Number	Company
HEMA	81723	Sigma (USA)
CQ	A009755501	Acros Organics (USA)
DMPT	A009614101	Acros organics (USA)

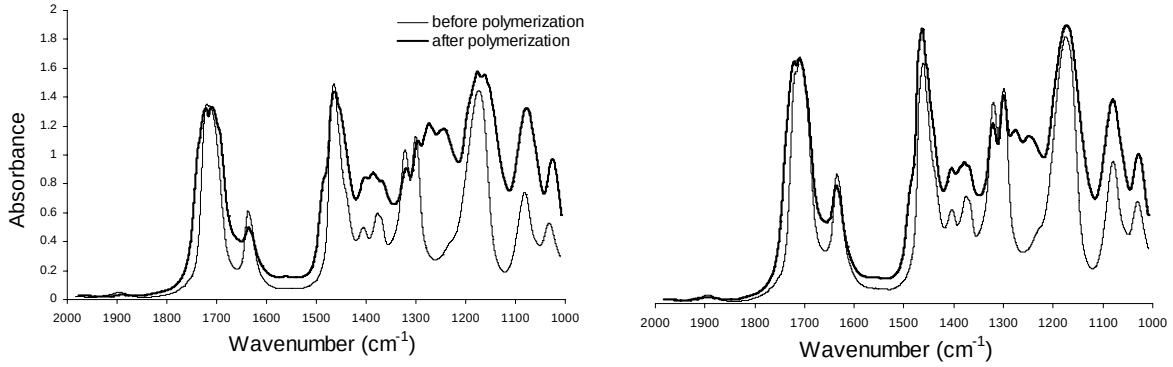

Fig 2. [left] IR spectra of solution 2 (4.76% water content) and [right] solution 3 (9.09% water content) before and after polymerization by 60s light curing.

cent of unreacted methacrylate groups was obtained as per the following equation:

$$(C=C)\% = \frac{[Abs(C=C)/Abs(C=O)]polymer}{[Abs(C=C)/Abs(C=O)]monomer}$$

The degree of conversion was obtained by subtracting the unreacted C=C% from 100%.
One way ANOVA and Tukey-HSD were carried out to compare and detect any differences among groups.

RESULTS

The remaining C percentage (mean), Coefficient of Variation (CV %), and Degree of conversion of different HEMA solutions were shown in Table 2. Figures 1-3 represent the infra-red spectra of HEMA solutions before and after polymerization. Moreover, C=C% remaining and DC% in different HEMA solutions were shown in Figures 4 and 5, respectively. A one-way ANOVA was performed at the 95% level of confidence on data. The results showed a considerable significant difference between groups (P<0.01). Tukey-HSD for comparison of means between different HEMA solutions showed that mean C=C % remaining of group 1 and group 2 did not show significant difference (P=0.196). Also group 4 and group 5 did not show any significant difference (P=0.904). A significant difference was obtained between other groups (P<0.001). A trend to decreasing the conversion was observed by increasing water in HEMA solution.

DISCUSSION

A significant amount of residual monomer remains unbound in restorative materials. Due to biocompatibility and the structural stability of the materials, it affects the mechanical properties such as tensile, compressive, and flexural strengths, elastic modulus, wear resistance, hardness, and creep [24].
The process of elution from restorative materials related to several factors. One factor relates to the amount of eluting substance, and this is

Table 2. HEMA solutions with different water content.

Number of solutions	HEMA ml	Distilled water ml (%)	(C=C)% Mean (SD)	Coefficient of Variation (%)	Degree of Conversion (%)
1	1.00	0.00 (0.00)	43.47 (7.44)	17.05	56.25
2	1.00	0.05l (4.76)	49.73 (4.87)	9.70	50.27
3	1.00	0.10 (9.09)	65.39 (3.79)	5.79	34.60
4	1.00	0.20 (16.66)	92.1 (3.55)	3.85	7.90
5	1.00	0.40 (28.57)	94.74 (2.33)	2.45	5.26

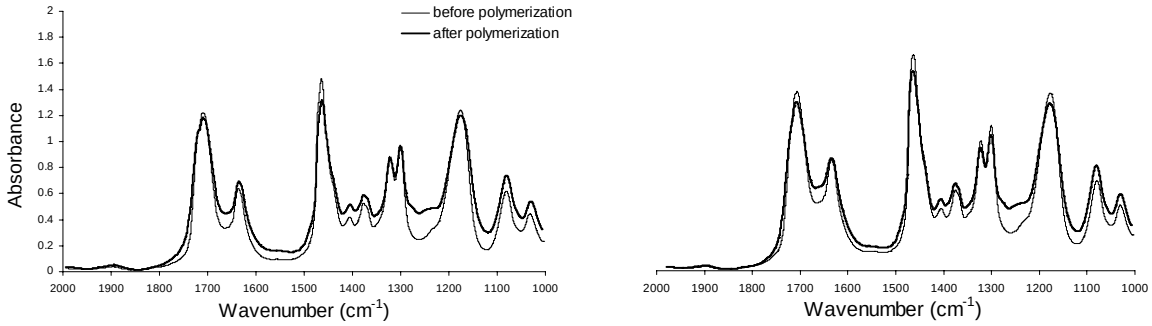

Fig 3. [left] IR spectra of solution 4 (16.66 % water content)and [right] solution 5 (28.57 % water content) before and after polymerization by 60s light curing.

directly related to the extent of the polymerization reaction, or the number of unreacted monomers. The higher the extent of polymerization reaction is responsible for lower residual monomers to be leached [25].

The extent of polymerization may be controlled by many factors, such as resin composition, specimen geometry, photo initiation concentration, irradiation intensity and duration, exposure to oxygen and curing temperature [26]. Degree of polymerization is one of the important factors may affect clinical performance of resinrestorative materials.

According to Imazato et al study, among several methods to determine DC of resins, Fourier Transform Infrared Spectroscopy (FTIR) has been proven to be a useful technique; also, it has been used as a reliable method [27]. Current study also showed that, the FTIR is proper instrument for determination of degree of conversion of HEMA in the bonding.

The absorbed IR spectra of HEMA consists of the following characterizations: The absorption bands at 1636 cm^{-1} represent the methacrylate C=C vibration. The band appearing at 1405 cm^{-1} is attributed to (=CH2). The 1463 cm^{-1} is assigned by methylene scissoring deformation (CH2) from the polythene plate, which overlapped with asymmetric methyl bending (CH3) at 1458 cm^{-1} band of HEMA. The band appearing in 1376 cm^{-1} is assigned by symmetrical methyl bending vibration from polythene plates. The bands appearing approximately at 1720 and 1175 are attributed to (C=O) and (C-O) respectively.

The bands of polythene plates in 1464 cm^{-1} and 1376 cm^{-1} did not interfere by the band of HEMA (C=O) at 1720 cm^{-1}. No interference was observed between the bands of polythene and the internal standard of HEMA.

The C=O frequency was approximately 1720 cm^{-1}. The C=O vibration was observed as a doublet in the spectra because the frequency of the C=O is affected by intra and intermolecular hydrogen bonding. In this system, because of the presence of water, hydrogen bonding occurred. As a result of this, the C=O appeared as a broadened doublet (~12 cm^{-1}). The effect of hydrogen bonding on the C=O vibration may affect its usefulness as an internal standard. However, whether the C=O vibration was a singlet or a doublet was not important since the shape of the bands did not change with conversion [28]. If hydrogen bonding occurs, it would involve a weak shift of the carbonyl (C=O) bond. In infra-red spectrum, frequency associated with carbonyls is generally not noticeably shifted by a hydrogen bond. In fact, the carbonyl peak is assigned to both non-bonded and H-bonded carbonyls. The effect of hydrogen bonding which gave rise to band broadening of the C=O vibration was eliminated by the use of integrated areas to calculate the intensity of this vibration [28].

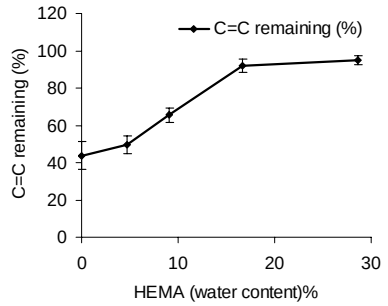

Fig 4. Comparison of C=C% remaining in different HEMA solution with a 95% confidence interval.

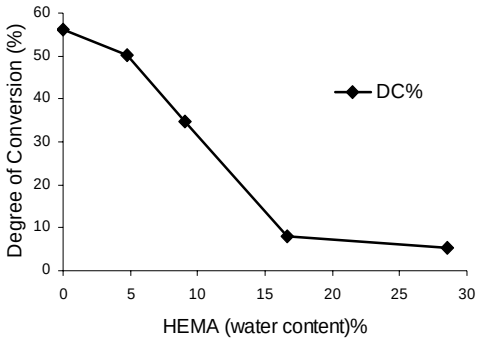

Fig 5. Degree of conversion of different HEMA solution.

In this study, when water was mixed with HEMA a broadened doublet occurred to the frequency difference of 12 cm^{-1}. Thus it was not meaningful to measure a peak height for the system. Therefore, determination of conversion was based on peak area. In addition, the shape of the C=O vibration bands (singlet or a doublet) did not change during the conversion. For reducing the effect of the hydrogen bond on the conversion calculation, for five HEMA solutions with different water content the following procedure was followed:

To obtain intensities for the vibration of interest, peak areas were measured. In each solution, the 1720/1636 peak ratio of cured polymer divided to average of the same peak ratio of uncured monomer of the same solution.

A trend of decreasing in HEMA conversion with increasing water observed in this study. According to Wang et al study, water has a major effect on HEMA conversion and decreases the conversion level of HEMA which is in agreement with our study [29]. The water/HEMA will polymerize less efficiently due to presence of water. The ratio (1636/1720) changes significantly within the 0.05 ml (4.76% water content) to 0.2ml (16.66% water content) water range for both baseline methods. However, the degree of conversion did not change after reaching 0.2 ml and before 0.05 ml. Our finding is in agreement with Jacobsen and Söderholm study, who reported the degree of conversion decreased to approximately 25% when the water content more than 0.2ml was added per ml resins. The most dramatic effect of water on the polymerization process occurs within a range, which exists under clinical conditions [30]. HEMA as a hydrophilic primer can copolymerize by the unfilled resin due to the light activator in unfilled resin. Although, a moist collagen mesh enhances primer infiltration [31], excess water can affect conversion of primer and unfilled resin.

An important requirement for fluid resins to obtain optimum bond strength is complete curing before placing composite resin over it. If the excess water did not remove before curing resin, this water contamination also could have dramatic effects on the bond strength [30]. The reason that the degree of conversion did not show significant result after reaching 0.20 ml and before 0.05 ml may be related to the hydrophilic nature of HEMA. HEMA may mix well with water but after increasing water content, it disperses in water, which may cause a decrease in conversion. At the 0.2 ml level, most of the HEMA molecules become separated, thus making them unable to polymerize [30].

CONCLUSION

The presence of remaining unreacted monomers can be a significant factor for decreasing

the degree of conversion and decreased by increasing water content.

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