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Effect of ultrasound on the setting characteristics of glass ionomer cements studied by Fourier Transform Infrared Spectroscopy

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Abstract
Objective: To investigate the effect of ultrasound (US) application on the setting of glass ionomer cement (GIC) by using Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) spectrometer. *Methods*: Two conventional GICs, Fuji IX Fast and Ketac Molar were studied. US application was started at 30 s or 40 s after mixing and was applied for times between 15 and 55 s on samples of two different thicknesses. The samples were analysed using ATR/FTIR.*Results*: US accelerated the curing process in both cements, US needed to be applied for more than 15 s. Both Fuji IX and Ketac Molar showed increased setting on increasing the US application duration from 15 s to 55 s. Increased setting of the GICs was produced when US application started 40 s after mixing rather than 30 s after mixing. *Conclusions*: The significant findings of the study include that US application accelerated the setting processes, by accelerating the formation of the acid salts. The salt formation increased with increase time of US application. The effect of application of US to setting GICs is influenced by time of the start of application of the US. The effects appear to material specific, with Ketac Molar showing a greater effect than Fuji IX.

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1 Introduction

Glass ionomer cement (GIC) is widely used as restorative materials in dentistry. They have also been used as bone cements in orthopaedic and ENT surgery because they are bioactive and promote bone growth [1] [2]. In dental applications the important properties are fluoride release, adhesion to tooth structure and negligible volume change during setting. These properties prevent bacterial microleakage and subsequent caries progression [3].

However, despite these advantages there are some disadvantages associated with GIC. They are moisture sensitive and have slow maturing processes so there are delays in the development of their final strength. GIC is also susceptible to fracture and has low wear resistance until fully matured [4] [5] [6]. Damage to the cement prior to complete setting leads to long term reduction in the strength of the GIC, thus accelerating the setting of GIC will overcome some of the disadvantages associated with slow setting. Currently GICs have generally been limited in use to the areas of low masticatory forces such as Class III and V restorations [7].

Some improvements have been made in their composition to overcome these problems and to gain a command set. These have included changes in the particle size of the glass phase, the molecular weight of polymer and the development of resin modified glass ionomer cements and cermets. These resin based modified materials have some of the benefits of conventional glass ionomer cements, such as good adhesion to tooth and fluoride release. However due to the presence of resin these systems also have disadvantages. The resin systems show polymerization shrinkage, monomer toxicity and poor long term mechanical properties particularly abrasion resistance as compared to conventional glass ionomer cements [7] [8].

It has been proposed that by applying US, the setting reaction of glass ionomer cements could be significantly accelerated and the early properties can be

substantially increased compared to traditional glass ionomer cements. By accelerating the maturation process, properties such as strength and resistance to water degradation immediately after placement of the filling will be improved. There are potential additional advantages in the use of US such as void reduction and better flow and adaptation of the cement to the cavity. Rapid setting allows a decrease in chair time, making restorations more convenient for both the patient and clinician, while also ensure that the patient can load the restoration sooner without risk of damage [8] [9].
The aim of the work reported here was to follow the setting of GIC when accelerated by the application of ultrasonic excitation and with special emphasis on analyzing the effect of ultrasound starting time and duration of US application after mixing on the setting of GIC.

2 Materials and Methods

Two conventional chemically cured capsulated GICs, Fuji IX (GC Corporation, Tokyo, Japan, lot number 0503081) and Ketac Molar (3-M ESPE, Seefeld, Germany, lot number 159219) were used. Both the cements consisted of an acid soluble calcium fluoroaluminosilicate glass powder and an acid liquid which is copolymer of itaconic and maleic acid. The powder and liquid are held in separate chambers in precise ratios in a capsule. The capsule is activated and mixed in a triturater. The equipment used for ultrasonically curing GIC was an EMS Piezon Master 400 dental scalar. The tip used for applying ultrasound is shown in Figure 1 and has a nominal tip diameter of 2mm. This ultrasonic equipment is routinely used by dentists for de-scaling purposes and it has a frequency between 25-30 kHz.

Figure 1: Tip used for ultrasound

Samples were prepared according to the manufacturer's specifications in a roto mixer (ESPE D-82229, Seefeld, Germany) and were injected in 3mm and 4mm deep cavities 3mm in diameter produced moulds manufactured from polyvinylsiloxane impression material. US was applied 30 or 40 seconds after mixing by placing the scaler tip on the top of the cement and applying light hand pressure to ensure the tip remained in contact with cement without causing any deformation. Five different durations 15, 25, 35, 45 and 55 seconds of US were applied. For each of variable, start time, duration and cement type, 3 repeat samples were prepared and analysed.

Samples were examined using a FTIR machine (Perkin-Elmer) in reflectance mode (Golden Gate) using PerkinElmer IR spectroscopy software. Immediately after cessation of the US application the moulds were placed on the FTIR machine with the side opposite to that where the US was applied facing the diamond window. The FTIR wavelength range was set between 1800 cm^{-1} and 700 cm^{-1}. To minimize the error 4 scan cycles were used for each reading. Before taking the sample readings, a background spectrum was obtained. This spectrum is a single-beam spectrum recorded without a sample on the machine, and used in ratio calculations for sample readings.
Spectra were generated at 2, 5, 10, 30 and at 60 minutes after the start of mixing for all the samples. For both cements the COOH peak was measured at 1700 cm^{-1} with COO^- peaks measured at 1600 cm^{-1} and 1410 cm^{-1} for Fuji IX and at 1560 cm^{-1} and 1405 cm^{-1} for Ketac Molar. Absorption spectra were obtained for the liquids of both Fuji IX Fast and Ketac Molar to compare with the spectra of setting cements and are shown in Figure 2 (a) and (b).

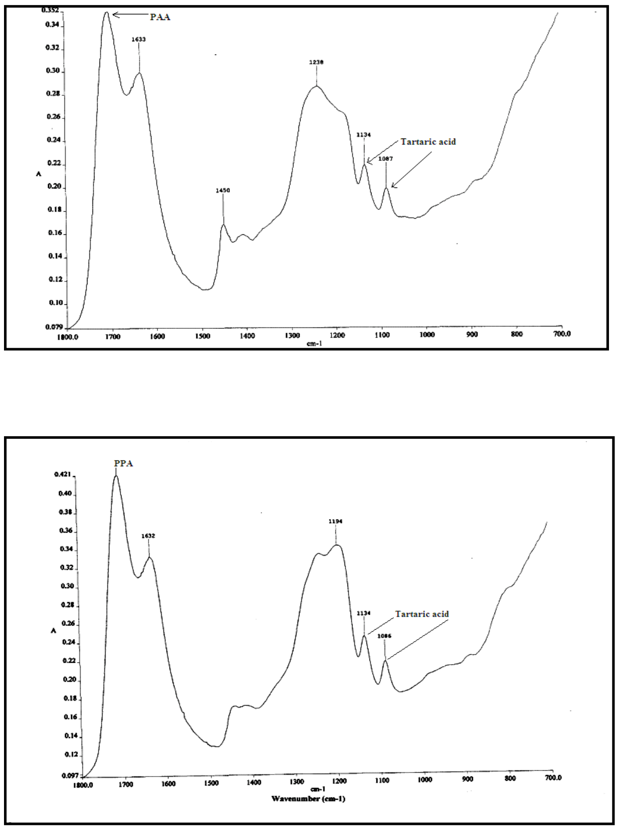
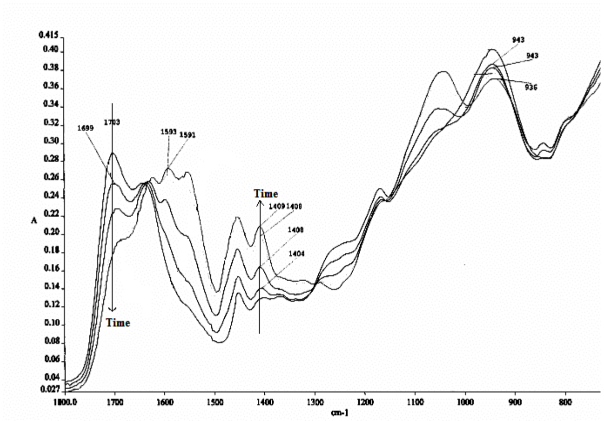


Figure 2: Spectra for the liquid phase of (a) Fuji IX and (b) Ketac Molar.

3 Results

3.1-Spectra for Non Ultrasound (NUS) Ketac Molar and Fuji IX Fast

Spectra were obtained at 2, 5, 10, 30 and 60 min after mixing samples of Fuji IX Fast and Ketac Molar set without the application of ultrasound (NUS) are shown in shown in Figs 3 (a) and (b). From the FTIR spectra the ratios of the heights of the 1600 to 1700 cm^{-1} and the 1410 to 1700 cm^{-1} peak were calculated for Fuji IX and heights of the 1560 cm^{-1} to 1700 cm^{-1} and the 1405 to 1700 cm^{-1} peak were calculated for Ketac Molar. The setting reaction tends to a reduction in the number of COOH groups as they set and reform as COO^- groups.



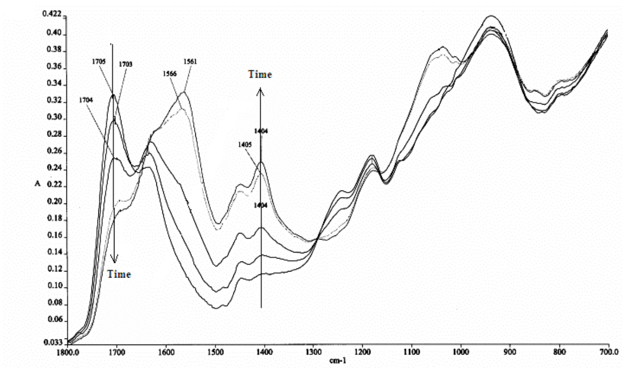


Figure 3: FTIR spectra for (a) Fuji IX and (b) Ketac Molar with no Ultrasound applied taken at 2, 5, 10, 30 and 60 min after mixing. The arrows indicate the increase or decrease in the heights of specific peaks with increasing time

From the spectra the ratios of the peaks 1600 cm^{-1} and 1410 cm^{-1} to the 1700 cm^{-1} peak were calculated for Fuji IX and the ratios of 1560 cm^{-1} and 1405 cm^{-1} to 1700 cm^{-1} for Ketac Molar and are show in Fig 4. At 2 and 5 minutes after mixing the peak ratios were higher for Fuji IX than Ketac molar, however at 30 and 60 minutes they were higher for Ketac Molar.

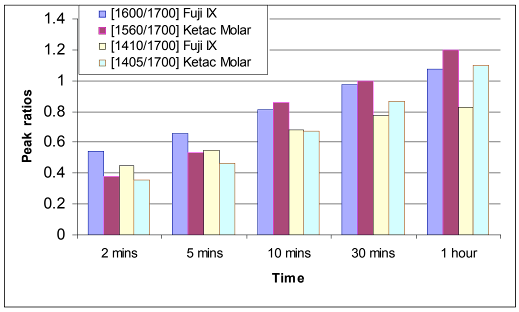


Figure 4: COO^-/ COOH ratios for Fuji IX and Ketac Molar with no application of US.

3.2- Effect of US Application

Fuji IX showed increased setting on the application of US. The effect of US was dependent on the duration of US applied. Applying US for 15 seconds increased the rate of reaction; however at the end of 60 minutes after mixing the difference between the setting of non-ultrasound samples and samples with 15 second US application was not significant as shown in Table 1. Like Fuji IX, Ketac Molar also showed higher setting rate on applying US and the setting was increased on increasing the duration of US as shown in Table 2.
The rate of setting increased with the increase in the duration of US application. Highest rate of setting was achieved on applying US for 55 seconds, the longest US application used in this study. When US was applied for 55 seconds, the peaks at 1700 cm^{-1} and 1405 cm^{-1} corresponding to COOH and COO^- respectively do not subsequently change much, indicating that polyacrylic acid (PAA) has already been neutralized by the ions from the glass phase and the cement is set.
after

Table 1 COO^-/ COOH ratios for Fuji IX at different times point after mixing with no ultrasound (NUS) and 15 (15s US), 35 (35s US) and 55 (55s US) seconds of ultrasound application after 30 seconds of mixing.

	NUS		**15 s US**		**35 s US**		**55 s US**	
Time [min]	(1600/ 1700)	(1405/ 1700)	(1600/ 1700)	(1405/ 1700)	(1600/ 1700)	(1405/ 1700)	(1600/ 1700)	(1405/ 1700)
2	0.544	0.444	0.864	0.602	1.102	0.853	1.388	1.102
5	0.661	0.549	0.886	0.625	1.164	0.866	1.404	1.113
10	0.809	0.676	0.977	0.713	1.187	0.913	1.416	1.133
30	0.977	0.777	1.070	0.790	1.218	0.967	1.409	1.128
60	1.073	0.830	1.09	0.831	1.236	0.997	1.419	1.136

Table 2 COO⁻/ COOH ratios for Ketac Molar at different times point after mixing with no ultrasound (NUS) and 15 (15s US), 35 (35s US) and 55 (55s US) seconds of ultrasound application after 30 seconds of mixing

	NUS		**15 s US**		**35 s US**		**55 s US**	
Time [min]	(1560/ 1700)	(1410/ 1700)	(1560/ 1700)	(1410/17 00)	(1560/ 1700)	(1410/ 1700)	(1560/ 1700)	(1410/ 1700)
2	0.379	0.358	0.695	0.510	1.274	1.113	1.417	1.134
5	0.533	0.463	0.834	0.585	1.399	1.128	1.444	1.157
10	0.855	0.671	0.986	0.714	1.411	1.130	1.459	1.168
30	1.000	0.864	1.159	0.879	1.419	1.145	1.487	1.171
60	1.200	1.100	1.226	1.222	1.436	1.157	1.499	1.182

Fuji IX samples showed higher $COO^-/COOH$ ratios when the US application was started at 40 s after mixing rather then at 30 s after mixing. The ratios for Fuji IX with US starting at 30 and 40 seconds time after mixing are shown in figure 5a, the total duration of US application was 25 s. Ketac Molar samples also showed higher $COO^-/COOH$ ratios when the US application was started at 40 s after mixing rather than at 30 s after mixing. The ratios for Ketac Molar with ultrasound starting at 30 and 40 seconds time after mixing are shown in figure 5b, the total duration of US application was 25 s.

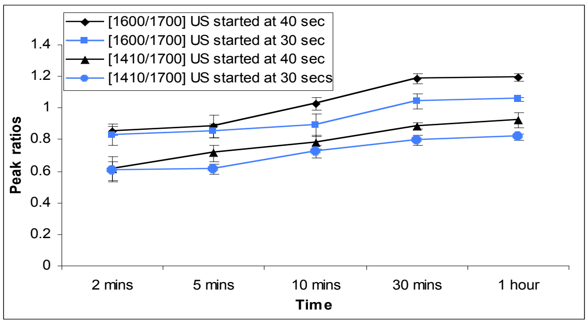


Figure 5a: Difference between $COO^-/COOH$ ratios of Fuji IX samples with US application started at 30 sec and 40 sec after mixing and applied for 25 seconds.

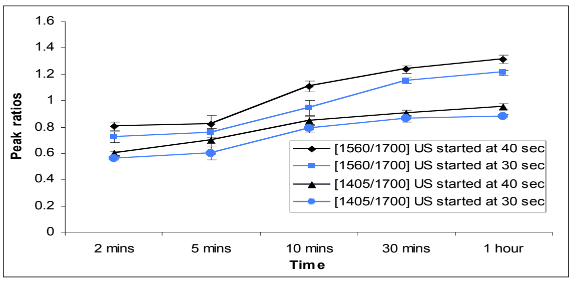


Figure 5b: Difference between $COO^-/COOH$ ratios of Ketac Molar samples with US application started at 30 sec and 40 sec after mixing and applied for 25 seconds

Applying US on both Ketac Molar and Fuji IX Fast increases their rate of setting, however the effect is greater in the case of Ketac Molar. On calculating the peak ratios two minutes after mixing and with various duration of US application it is obvious that Ketac Molar has enhanced set compared to Fuji IX Fast. However in the case of 15 s US application, the peak ratios at two minutes are higher for Fuji IX Fast, as shown in Figure 6a.

When the ratios are obtained at 60 min after mixing, they clearly show increase setting for Ketac Molar than Fuji IX even with only 15 s of US. This also supports the fact that as the time increases the COO^- groups increase implying salt formation becomes more enhanced in Ketac Molar, as shown in Figure 6b.

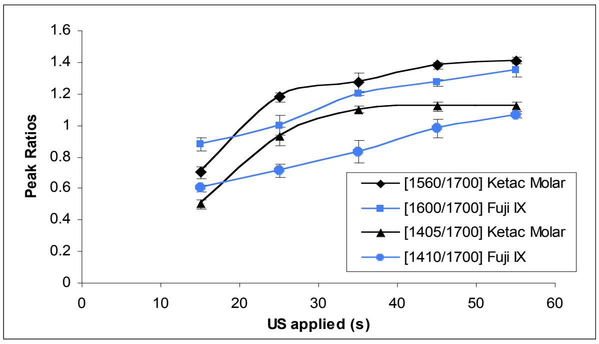


Figure 6a: Peak ratios for Fuji IX Fast and Ketac Molar at 2 min after mixing with different durations of US applications.

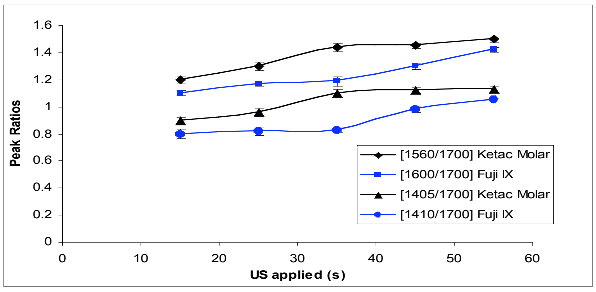


Figure 6b: Peak ratios for Fuji IX Fast and Ketac Molar at 60 min after mixing with different durations of US applications.

3.3- Effect of Section Thickness

FTIR readings were taken on the opposite side of the sample to which US was applied. To determine the penetration of US two thicknesses of the samples were used. Results showed high $COO^-/COOH$ ratios thus increased setting for 3mm samples ratios and neutralization of PAA at the end of 60 min after mixing as compared to 4mm samples. As shown in the figure 7a the ratios for 3mm samples are higher than for 4mm samples on applying US for 35 seconds.

Higher ratios were achieved for Ketac molar samples with 3mm thickness as compared 4mm thick samples as shown in figure 7b.

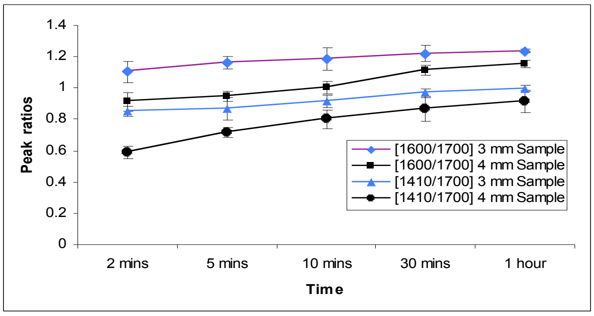


Figure 7a: Difference between $COO^-/COOH$ ratios of 3 and 4 mm thick Fuji IX samples with 35 seconds US application.

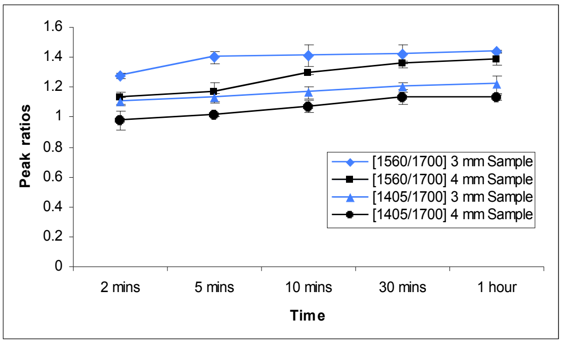


Figure 7b: Difference between $COO^-/COOH$ ratios of 3 and 4 mm thick Ketac Molar samples with 35 seconds US application

4 Discussion

Increased rate and degree of setting was observed with increase of US duration from 15 to 55 seconds. The setting of the cements was higher when the US application was started at 40 s after mixing compared to starting 30 s after mixing, this finding has not been reported previously. This result shows that allowing the cement to set chemically for longer before application of US causes an increase production of COO^- groups in the cement which on application of US crosslink to give increase COO^- ratios.

Both Fuji IX and Ketac Molar showed higher rates of setting after applying US for atleast 35 seconds. However the effect of US is more pronounced on Ketac Molar as compared to Fuji IX as shown in Figure 6(a). This figure shows the ratios at 2 minutes after mixing with different duration of US applied, it is obvious that the US has a greater effect on Ketac Molar at all US durations greater than 15 seconds. This supports the hypothesis that Fuji IX Fast sets faster during the initial minutes than Ketac Molar, as applying US for 15 s does not really affect and enhance the setting of this cement. At the end of 60 minutes after mixing and with different durations of US application Ketac Molar show higher values and thus increased setting as compared to Fuji IX as shown in Figure 6 (b).

The effect of US was measured by placing the cement samples on the FTIR lens. The surface facing the FTIR lens was the surface opposite to the surface on which the US was applied. Thus to investigate the effect of thickness on penetration of US, US was applied to both 3 and 4 mm thick samples. Greater setting was observed for 3mm samples as compared to 4mm samples with all US application durations and with both starting time of 30 seconds and 40 seconds after mixing as shown in figure 7 (a) and (b). This tends to suggest that the effects of US are depth dependent, the greater the depth, the weaker effect of US at the bottom. However clinically the requirement is to set the occlusal surface quickly and to the grater extent possible as the cement below the surface layer and within the tooth surface is less prone to moisture and desiccation.

Applying US not only increases the setting reaction of GICs, it also improves the mechanical properties of GIC [7]. The compressive strength and surface hardness of GIC has been shown to be increased by the application of US and creep can be minimized [8] [10]. Enhanced bond strength between GIC and enamel can be achieved by the application of US [11].

US application can be easily applied in dental clinics as it does not require any special instrument and can be applied by dentists using ultrasonic equipment used for scaling available in most of the dental clinics.

5 Conclusions

Ultrasound application accelerates the formation of the acid salts. The salt formation increased with increase time of US within the times investigated in this study.

The effect of application of US to setting GICs is influenced by time of the start of application of the ultrasound. The effects appear to material specific, with Ketac Molar showing a greater effect than Fuji IX.

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