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CHAPTER 4

The influence of environmental conditions on the material properties of setting glass ionomer cements

Dent Mater 2006 22:852-856

4.1 Abstract

The aim of this study is to investigate the influence of temperature on the setting time and compressive strength of two conventional glass ionomer cements (GICs) and to determine the influence of storage medium, oil or water, and storage time.

Two conventional GICs, Ketac Molar (3M-ESPE Dental Products, Seefeld, Germany) and Fuji IX Fast (GC Corp., Tokyo, Japan) were used to perform flow property tests and compression tests. Flow property measurements were performed using a displacement rheometer at six different temperatures. From the results of the rheometer tests the working times and setting times could be determined. The specimens for the compressive tests were stored at four different temperatures and in two different media. Testing took place at five time intervals reaching from one hour to three months.

The results of the rheometer tests showed that a temperature increase speeded up the setting reaction significantly. The compressive strength results showed a jump in time as a result of the higher curing temperature but no long-term strength effect was observed. Materials curing in oil reached a significantly higher compressive strength compared to those stored in water and Fuji IX Fast is significantly stronger than Ketac Molar.

It was concluded that a temperature between 60°C and 70°C almost sets conventional GICs on command and improves the early compressive strength.

4.2 Introduction

The chemical adhesion to enamel in combination with the fluoride-releasing property and its excellent biocompatibility gives glass ionomer cements (GICs) an important place in the today's dental practice. GICs are used as temporary or permanent restorative material, as luting material for crown and bridgework, and in orthodontics for cementing bands and brackets. Since the introduction in 1971 of the first ASPA GICs by Wilson and Kent (1) major improvements have been made, but some disadvantages of the GICs still remain.

Basic knowledge of the setting reactions and its kinetics will give an understanding of the properties of these cements. GICs are comprised of an aqueous polyalkenioc acid and an alumino-silicate glass component. After mixing, H^+-ions split off the COOH-groups from the acid-chains and react with the glass particles. Due to a partial dissolution, the outer surface of the glass particles is converted into a gel coat from which Al^{3+}, Ca^{2+} and F^- ions are secreted. The COO^- groups and the released $Al^{3+}$and Ca^{2+} ions enables cross linking of these chains, giving a solid network around the glass particles. The binding of the COO^- groups with Ca^{2+} ions from the enamel occurs and a chemical bond between the cement and the tooth structure is achieved. During these reactions fluoride ions are released from the glass, which can have antibacterial effects (2) and are able to be built into remineralising hydroxyapatite crystals.(3, 4) The cross linking reactions are slow and it takes a long time before the cements are completely matured. During this period the material is vulnerable to external attacks such as saliva or water, which dissolute and dissolves the material.

Because of these drawbacks, Antonucci introduced the first resin modified glass ionomer cement (RMGIC).(5, 6) This hybrid cement contains, beside the glass ionomer cement, 4.5% to 6% HEMA and/or Bis-GMA. The resin part cures 'on command' by which some of the above mentioned problems are avoided.

Besides adding resin to the GICs, the setting of the cement can also be influenced by external factor such as pressure, temperature, humidity and mixing time.(7, 8) In the oral cavity it is difficult to control these variables although there are some solutions. The free surface of a restoration can be covered preventing it from saliva contamination and in principle the temperature can be influenced by external sources. It has been shown that the setting period can be shortened when energy, for instance in the form of heat, is applied to the setting material.(9, 10) A quantification of this effect and the effects on other material properties are as yet unknown.

The purpose of this study is to determine the influence of temperature on the working and setting times of two commercially available conventional GICs, Fuji IX

Fast and Ketac Molar. Furthermore, the influence of temperature and storage medium, oil or water, on the compressive strength of the same materials was investigated at different time intervals over a period of three months.

4.3 Materials and Methods

The two materials used in this study are listed in Table 4.1 by product name, manufacturer, colour, batch number, and expiry date.

Table 4.1 Materials used in this study.

Material	Manufacturer	Colour	Batch no.	Expiry date
Fuji IX Fast	GC Europe, Leuven, Belgium	A3	0206284	2004-06
Ketac Molar	3M-ESPE, Seefeld Germany	A3/U	133889	2005-02

Rheological measurements

The working and setting times were determined with a displacement rheometer (ACTA; Amsterdam, the Netherlands) (11). A 9 mm diameter stainless steel cylinder and a glass bottom plate assembly with a gap width of 0.1 mm was used in the time-oscillation at a frequency of 0.17 Hz at a 1.15 degree rotation. The temperature of the bottom plate was controlled by a Peltier device in order to maintain the specimen at the desired temperature. Before the initiation of a run, the upper cylinder was brought into contact with the glass plate to equilibrate the temperature of the 2 plates. Furthermore, the bottom plate and the cylinder were isolated from external influences in an isolation box. Close to the specimen the temperature was measured with a calibrated TC-08 data logger (Pico Technology Limited, St Neots, UK). The amplitude of the oscillating cylinder was measured 10 times per second and the data were recorded on a computer using Labview 5.0 (National Instruments corp., Austin, Texas, USA) for a maximum time period of 15 minutes. The materials were placed in the rheometer according to the following protocol. The encapsulated GICs were activated and mixed according to the manufacturers instructions in a Silimat 5S (Vivadent; Schaan, Liechtenstein). At the moment of activation the time was recorded and the temperature and rheological measurements commenced. After mixing, the material was transferred directly into the rheometer.

The tests were performed at six different temperatures, 20, 30, 40, 50, 60 and 70°C respectively and repeated 3 times for each temperature. The working time was defined as the time between the start of mixing and the initial observation of displacement. For practical reasons this point was set at 5% of the initial amplitude of the rheometer. Setting time was defined as the time at which a material achieved less than 95% of its maximum displacement.(12)

Compressive strength determination

Compressive strength was determined with Hounsfield H109KM universal testing machine (Hounsfield, Redhill, UK) at a crosshead speed of 0.5 mm/min. The specimens were prepared according to the following procedure. After activation of the capsules, mixing of the material was performed according to the manufacturers instructions in a Silimat 5S (Vivadent; Schaan, Liechtenstein) for 10 seconds. Thereafter the material was injected in a stainless steel cylindrical mould with a diameter of 3.15 mm and a height of 5.0 mm. The free surfaces were covered with a polyester strip on which a gentle force was applied, ensuring a parallel upper and lower surface to the specimen.

Five minutes after activation of the capsule, the specimens were removed from the mould and placed in paraffin oil (Merck KGaA, Darmstadt, Germany) or tap water. The specimens were stored at four different temperatures, 20°C, 37°C, 50°C, and 70°C. The specimens were then tested at 5 different time intervals, 1 hour, 1 day, 7 days, 4 weeks and 3 months, making a total of 80 groups. Each group consisted of 8 specimens, which makes a total of 640 specimens.

Statistical analysis

The results of the compressive strength tests were statistically analysed using 4-way ANOVA. For the rheometer test results a 2-way ANOVA was executed with temperature as the dependent factor. The independent sample t-test was used for the comparison between the materials. For both ANOVA's the *post hoc* analysis was performed with the Tukey HSD test at a P-level of 0.05. The software used was SPSS 11.0 (SPSS inc., Chicago, USA).

4.4 Results

Results of the rheometer tests of Fuji IX Fast as a function of time for the different temperatures are shown in Figure 4.1. The plotted points at each time are the average of the results of the 3 repeated runs. The error bars are determined by the

standard deviation of this data at each time. The results of Ketac Molar are very similar.

The average working and setting times together with the standard deviations are summarized in Table 4.2. Two-way ANOVA showed that Fuji IX Fast gave a significantly shorter curing time compared to Ketac Molar ($F = 93.9$, $P < 0.001$) When this is split into working and setting times the significant differences remained (respectively $F= 4.4$, $P= 0.047$ and $F= 99.5$, $P<0.001$). However, for the working time the mean difference was 7 seconds, which in not considered to be clinically significant. The mean setting times of the materials varies around 60 seconds. This is approximately 30% of the total mean setting time and therefore clinically significant.

The comparison of the environmental setting temperatures showed that with every 10°C increase the working and setting time significantly shortened. Only after 60°C was there no difference in all groups, compared to the 70°C.

Figure 4.2 shows the plots of the temperature dependence of the working time for Fuji IX Fast and Ketac Molar. The data are presented as Arrhenius plots in which the logarithm of the reciprocal working or setting time is plotted against reciprocal absolute temperature. Since the setting of GICs is a complex process with a sequence of steps, such a plot should give a straight line. From the slope of this line the molar activation energy of the rate-determining step in the sequence can be derived. For the working time of Fuji IX Fast and Ketac Molar these plots were found to be linear, and from the slope an activation energy of 27.3 KJ/mol, and 30.2 KJ/mol, respectively, could be calculated. For the setting time an activation energy of 34.2 KJ/mol, and 37.5 KJ/mol was found for Fuji IX Fast and Ketac Molar, respectively.

Table 4.3 shows average compressive strength together with the standard deviation for Fuji IX Fast and Ketac Molar measured after different storage time and temperature. Four-way ANOVA showed significant differences between the materials, temperatures and storage times as well as for the storage medium. Specimens stored in oil were significantly stronger than specimens stored in water ($F = 486.3$, $P<0.001$). Fuji IX Fast is significantly stronger than Ketac Molar ($F = 364.0$, $P<0.001$). The *post hoc* analysis of the compressive strength is summarized in Table 4.3. In this table the results are horizontally analysed for the differences in temperature and vertically for the differences in storage time.

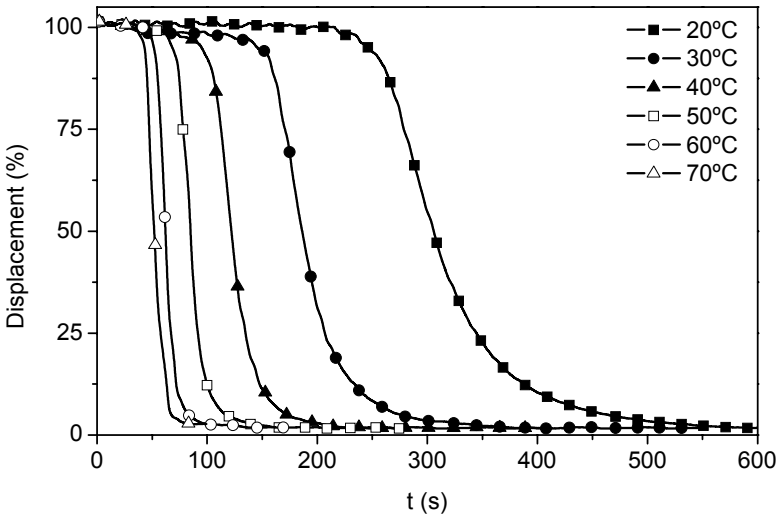

Figure 4.1 Graphical representation of the influence of environmental temperature on the change in viscosity with the setting time of Fuji IX Fast determined with the displacement rheometer. From these graphs the 5% and 95% settings could be determined as the measure for the working and setting time.

Table 4.2 The average working and setting times together with their standard deviations, measured at different temperatures.

T (°C)	Working time (s)		Setting time (s)	
	Ketac Molar	Fuji IX Fast	Ketac Molar	Fuji IX Fast
20	260.7 (14.3)[a]	230.0 (30.3)[a]	669.2 (40.4)[a]	449.4 (38.7)[a]
30	158.2 (3.4)[b]	137.8 (7.1)[b]	342.6 (16.6)[b]	273.9 (10.5)[b]
40	84.7 (1.6)[c]	89.9 (6.0)[cd]	199.5 (5.4)[c]	170.8 (10.0)[c]
50	65.9 (2.8)[d]	67.3 (2.4)[de]	140.7 (6.7)[d]	117.8 (6.5)[d]
60	52.1 (3.0)[de]	52.4 (1.6)[e]	93.1 (3.2)[de]	82.4 (2.7)[de]
70	43.8 (1.0)[e]	45.1 (2.7)[e]	69.7 (4.0)[e]	65.4 (5.6)[e]

Equal characters mean that there is no significant difference between different temperatures.

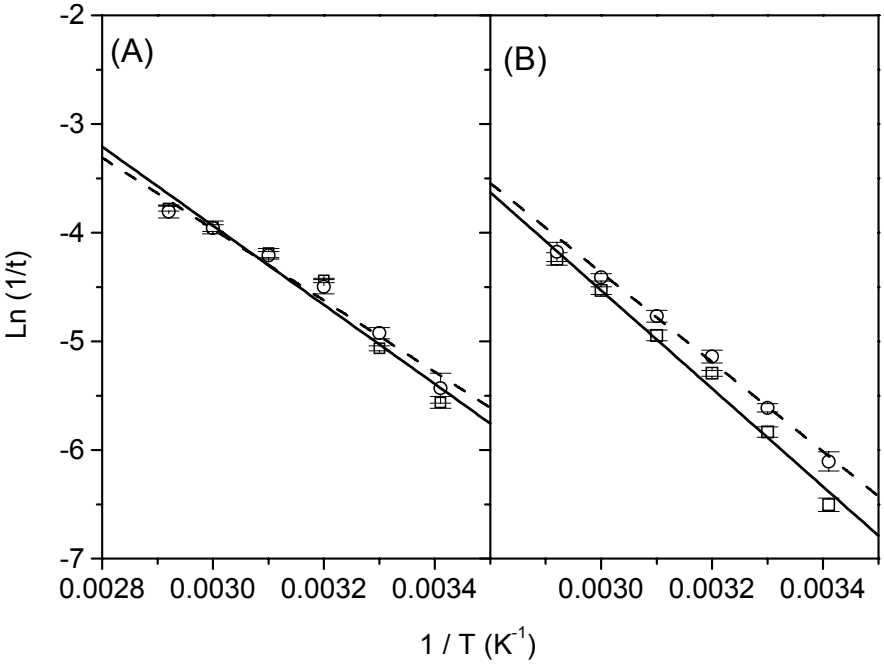

Figure 4.2 The Arrhenius plot of ln (1/t) against 1/T (K^{-1}) show the best fitted straight line of the setting of Fuji IX Fast (dashed line) and Ketac Molar (solid line). The left graph shows the results for the working time; on the right the setting time is shown.

4.5 Discussion

In this *in vitro* study the compressive strength and setting properties of Ketac Molar and Fuji IX Fast in relation to different environmental conditions were studied. The temperature variation, the influences of storage medium, and storage time were investigated.

Differential Thermal Analysis (DTA) (13), the in the standard for water-based cements described penetration method (ISO 9917:1991E), and the displacement rheometer test (11), are most commonly used to describe the setting properties of GICs. The DTA method measures the temperature of the setting material. The time between the start of mixing and the start of the exothermic reaction is considered to be the working time. The setting time is determined as the period between the start of mixing and the exothermic top. At this stage the setting reaction is not fully completed. If the temperature decreases to 5% of its exothermic top the setting reaction can be considered as ended.(14) The ISO 9917 penetration test measures only the setting time by using a flat-ended indenter. If this device fails to make a complete indentation the setting time is achieved. These tests are performed at 37˚C and with a humidity of

90%. The visco-elastic properties can also be studied with a displacement rheometer as described in the materials and methods section.

Table 4.3 The average compressive strengths (MPa) together with their standard deviations of the two materials (KM = Ketac Molar and FIXF = Fuji IX Fast), their storage conditions and the different time intervals.

		20°C	37°C	50°C	70°C
FIXF	1h	95.0 (5.0)^{aA}	127.3 (15.3)^{aB}	178.7 (11.1)^{aC}	181.5 (21.7)^{aC}
Oil	1d	158.9 (23.1)^{bA}	178.9 (14.7)^{bAB}	192.3 (22.4)^{abBC}	208.3 (21.2)^{abC}
	1w	180.5 (16.3)^{bcA}	196.4 (29.9)^{bA}	208.5 (23.6)^{abAB}	241.9 (39.8)^{bB}
	4w	203.2 (27.8)^{cA}	200.5 (34.9)^{bA}	223.8 (33.6)^{bA}	211.1 (22.5)^{abA}
	3 m	183.1 (27.8)^{bcA}	198.3 (23.1)^{bAB}	229.7 (33.6)^{bB}	215.3 (33.6)^{abAB}
KM	1h	93.0 (9.6)^{aA}	93.7 (15.6)^{aA}	144.9 (28.3)^{aB}	141.3 (26.4)^{aB}
Oil	1d	134.6 (19.8)^{aA}	150.3 (26.4)^{bcAB}	175.1 (32.5)^{abcB}	159.0 (28.3)^{aAB}
	1w	156.5 (29.3)^{bcA}	145.0 (19.7)^{bA}	160.1 (33.0)^{abA}	146.9 (31.5)^{aA}
	4w	184.2 (22.0)^{bAB}	183.9 (28.6)^{dAB}	210.9 (32.6)^{cB}	174.2 (10.3)^{aA}
	3 m	183.2 (34.8)^{bAB}	181.2 (22.5)^{cdA}	194.4 (37.0)^{bcAB}	224.3 (27.3)^{bB}
FIXF	1h	65.8 (11.1)^{aA}	102.1 (8.4)^{aB}	131.9 (21.5)^{aC}	154.1 (16.4)^{aD}
Water	1d	149.2 (25.0)^{bA}	168.4 (14.5)^{bAB}	182.2 (19.5)^{bB}	189.2 (21.4)^{bB}
	1w	159.1 (28.7)^{bA}	182.5 (35.4)^{bA}	165.1 (31.3)^{abA}	168.1 (10.4)^{abA}
	4w	160.4 (29.6)^{bA}	177.9 (13.9)^{bA}	173.6 (35.9)^{bA}	175.4 (32.8)^{abA}
	3 m	141.4 (25.5)^{bA}	173.0 (21.1)^{bB}	150.2 (17.6)^{abAB}	158.8 (26.7)^{abAB}
KM	1h	53.5 (7.3)^{aA}	71.1 (10.9)^{aB}	60.6 (15.7)^{aAB}	64.3 (15.4)^{aAB}
Water	1d	83.8 (11.6)^{bA}	112.3 (19.1)^{bB}	134.8 (15.3)^{bBC}	137.8 (21.8)^{bcC}
	1w	110.8 (14.2)^{cdA}	118.2 (10.9)^{bA}	127.5 (23.8)^{bAB}	147.9 (22.0)^{bcB}
	4w	127.8 (15.5)^{dA}	122.5 (14.7)^{bA}	138.3 (25.5)^{bA}	170.6 (31.0)^{cB}
	3 m	98.0 (12.2)^{bcA}	122.0 (25.6)^{bAB}	136.3 (20.1)^{bB}	121.0 (26.0)^{bAB}

Statistical differences were calculated using the Tukey HSD *post hoc* analysis. The capital characters show the statistical differences between the temperatures (horizontal). The small characters indicate the statistical differences between the times (vertical). Equal characters mean that there is no significant difference. $P<0.05$ was considered as statistically significant.

Although these tests all measure different properties, the setting time can be determined with all three of them. The working time can be measured with use of the DTA test and the displacement test but not with ISO 9917 penetration test. Because of

the different nature of the tests, the obtained working and setting time may differ. A study of Kilpatrick *et al.* reports that the ISO 9917 method underestimates the setting time by up to 32% compared to the DTA method.(14) With the consideration that the DTA method determines the setting time as the top of the exothermic reaction and not at the end of the chemical reaction the material might still be displaceable. It is therefore likely that the displacement method gives higher outcomes compared to the DTA method. According to the manufacturers the setting times of Fuji IX Fast and Ketac Molar measured with the ISO 9917 method at 23°C are 120 s and 270 s, respectively. This setting time is much shorter than the setting time obtained with the rheometer in this study, 449 s and 669 s at 20°C, respectively, but in line with the explanation given above.

The results from the rheometer showed that working and setting time decreased with increasing temperature. The Arrhenius plot (Figure 4.2) showed that for Ketac Molar and Fuji IX Fast the lines for the working and setting times are almost parallel, giving nearly the same activation energy for both processes. This means that the reaction processes involving the working and setting time originate most probably for the same rate-determining step in the maturing reactions of the cements. A logical explanation would be the cross linking of polyalkenioc acid chains by Ca^{2+}.(15)

The question is raised if 'on command set' could be achieved for GICs by applying an external heat source. Although no clear definition of a setting on command is available at present it can be said an ideal material will not react at mouth temperature, but is fully matured after 20 to 40 s application of an external heat source. In other words, the working time should be as long as possible at 37°C and the activation energy should be of a magnitude that will set the cement within 20 – 40 s at a clinical acceptable temperature. That application of external heat enhances working and setting time significantly can be seen in the Table 4.2. From a clinical point of view the working time at 37°C and the activation energy of both GICs are nearly the same, and therefore not much difference is expected in 'on command set' behaviour of these two materials.

The specimens stored in oil showed significantly higher compressive strength values compared to those stored in water. The explanation for the lower strength results in the water groups is the dissolution of the surface of the specimens and the surface one of the parts which is responsible for the maximum force resistance until fracture.(16) The influence of storage medium on the compressive strength of GICs confirms previous reported data.(16, 17) Increasing temperature resulted always in a higher compressive strength after one hour, expect for Ketac Molar stored in water.

The deteriorating effect of water on the compressive strength of Ketac Molar is of larger influence than the faster setting achieved by the higher temperature. It was already shown by de Gee *et al.* and van Duinen *et al.* that the first 24 hours are very critical in GIC setting. The material is in this period most prone to wear and dissolution.(18, 19) If this vulnerable period can be shortened as a result of a faster setting time these properties might be positively influenced as well.

From the literature it can be concluded that adding energy to setting GIC, in the temperature range as researched here, will not harm the pulp.(20) Nevertheless, due to the fact that in the clinic energy is already applied using ultrasound, some reservations have to be made with respect to the application time and distance of the heating device to the pulp. More research has to be done to make sure that heat can be applied safely in the clinic.

4.6 Conclusions

- The working times of Ketac Molar and Fuji IX Fast are almost equal. Both materials react equally on the application of heat.
- A temperature between 60°C and 70°C, applied during setting, gives a significantly higher initial compressive strength and reaction speed, resulting in an almost “on command” curing for both materials.
- Storing temperature, storage time and storage medium have a significant influence on the compressive strength of Ketac Molar and Fuji IX Fast. This should be taken into consideration when using these materials either in the clinic or for research purposes.

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