ELSEVIER
Thermochimica Acta 382 (2002) 161–168
thermochimica acta
www.elsevier.com/locate/tca

Thermometric monitoring of setting biomaterials

R. Zimehl[a,*], J. Drews[b], H. Fischer-Brandies[b]

[a]Institute for Inorganic Chemistry, Christian-Albrechts-University, Olshausenstr. 40, D-24098 Kiel, Germany
[b]Clinic for Orthodontics, Christian-Albrechts-University, Arnold-Heller-Str. 16, D-24105 Kiel, Germany

Received 3 May 2001; accepted 8 June 2001

Abstract

The setting reaction of different dental glues, i.e. conventional glassionomer cement (GIC), resin modified glassionomer cement (RMGIC) and composite adhesive were investigated with the thermal activity monitor (TAM). The water content of the materials and the water activity in the specimens were determined with isopiestic measurements after different setting periods. The information extracted from the thermochemical analysis for the setting reaction at different time intervals were further correlated with the material balance of the setting biomaterial. In respect to the practical application of the materials in dentistry we discussed the formation and the mechanical strength of the interfacial layer formed between enamel and orthodontic attachments. The study clearly revealed that the use of the aforementioned techniques, namely calorimetric, adsorption measurements, and the combination with microscopy and spectroscopic techniques is a suitable tool in examining the setting process of dental material. The study further elucidate information on several aspects of bonding orthodontic attachments with GIC to enamel surfaces, evaluation of material properties, future developments of biomaterials and related dental materials for orthodontic, conservative and restoring strategies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Micro-calorimetry; Biomaterials; Glassionomer cements; Water adsorption; Dental enamel

1. Introduction

Irregularities in the alignment of teeth (Fig. 1a) can cause fundamental suffering for humans and other creatures. This is due to not only on cosmetically grounds but more serious, because of orthopaedic reasons. But even for adults it is nowadays possible to correct the alignment by fixing orthodontic attachments to the disproportionate teeth (Fig. 1b). The orthodontic attachment is fixed to the tooth enamel by dental adhesives (composite resins). Composite resins are clinically well-proven dental materials which were developed at the beginning of the 1960s. The fixation of the orthodontic attachment by dental adhesives implies the conditioning of the dental enamel, typically by etching the enamel surface with 30–50% phosphoric acid [1–3]. The formation of the so-called etching patterns enables the dental glue to penetrate deeply into the porous enamel surface. These polymer cones are responsible for the retentive adhesion of the dental attachment. But surface etching also sacrifices healthy dental enamel and moreover, dental diseases like secondary caries and periodontitis can be caused and intensified by the orthodontic attachments.

The development of secondary caries and periodontitis is intimately linked to the structure of the tooth hard substances namely, enamel and its interaction with the oral environment, saliva and different microorganisms. The surface of the teeth is characterised by a crystallised arrangement of mineral components

---

[*] Corresponding author. Fax: +49-431-880-1608.
E-mail address: r.zimehl@email.uni-kiel.de (R. Zimehl).

PII: S0040-6031(01)00726-2

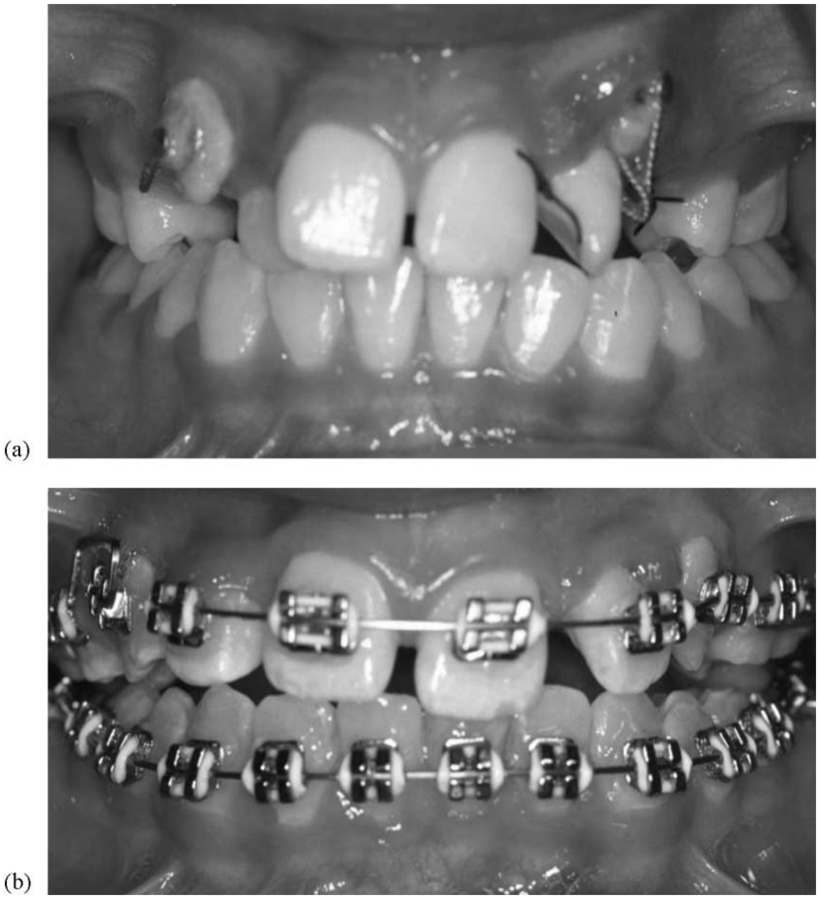


Fig. 1. Extremely disproportionate dentition: (a) before orthodontic treatment; (b) after fixation of orthodontic attachments. Note the application of metal brackets directly on the enamel surface.

with incorporated and chemisorbed biopolymers. The dental enamel is highly mineralised. About 96% of weight consists of tightly packed hydroxyapatite crystallites with 1% being organic molecules and 3% being water [4,5]. Furthermore, the dental enamel is covered by a protective protein layer [6–8]. However, even the enamel covered by the natural protective layer and much more the bare enamel is sensitive to acid attack. Thus, it is very advisable to minimise the treatment of the enamel surface with respect to preserve as much enamel as possible in order to avoid enormous costs for the public health care organisations caused by the secondary dental diseases.

A step towards this direction arose with the development of the so-called glassionomer cements (GICs) [9,10]. By introducing modern dental glues for the fixation of orthodontic attachments the risk of damaging the healthy enamel surface was minimised. The orthodontic treatment was further improved by the development of the resin modified glassionomer cements (RMGICs) [11,12] and its application with metal and ceramic brackets. The major advance in the GIC is its ability to adsorb permanently to the surface of hard oral tissues. Bond strength with GICs may be enhanced by cleaning organic debris off enamel surfaces with polyacrylic acid [13,14]. Another advantage of GICs is constant fluoride release, which inhibits secondary caries [15,16].

With this study we want to report several aspects of the bonding of orthodontic attachments with GICs to enamel surfaces. First we used calorimetric and water-vapour adsorption measurements as a tool to examine the setting process of dental material. Then by combining the results from the aforementioned techniques with results derived by different microscopic and spectroscopic techniques we will further discuss details of the molecular interaction at the dental enamel surfaces.

2. Experimental

2.1. Materials

The biomaterials tested were two conventional GICs, Aqua Meron (Voco GmbH, D-27457 Cuxhaven) and AquaCem (DeTrey Dentsply, D-78404 Konstanz), two RMGICs, Photac-Bond Aplicap and Photac-Fil Aplicap (both from ESPE-GmbH, D-82227 Seefeld/Oberbayern) and a conventional composite material, Concise Orthodontic Bonding (3M Medica GmbH, D-46325 Borken), which was used as reference.

2.2. Methods

The curing reaction of the dental adhesives were recorded by the thermal activity monitor (TAM, Thermometric AB, Järfälla, Sweden). We used the so-called ampoule technique to follow up the heat evolution of the setting biomaterial. The flow-chart diagram of the experimental procedure is depicted in Fig. 2. In a typical experiment the samples of GIC material were prepared outside of the micro-calorimeter in an air-conditioned room according to the manufacturers instruction. After the appropriate mixing of the components approximately 0.08–0.21 g of the biomaterial was quickly transferred to the glass ampoule. The ampoule was tightly sealed with the delivered clamps and then brought to the calorimeter for temperature equilibration [17]. After 10 min equilibration time the ampoule was adjusted at the measuring position of the micro-calorimeter and the heat flow-rate was continuously recorded as a function of time [18]. The standard deviation for most of the calorimetric measurements varied between 2 and 5%.

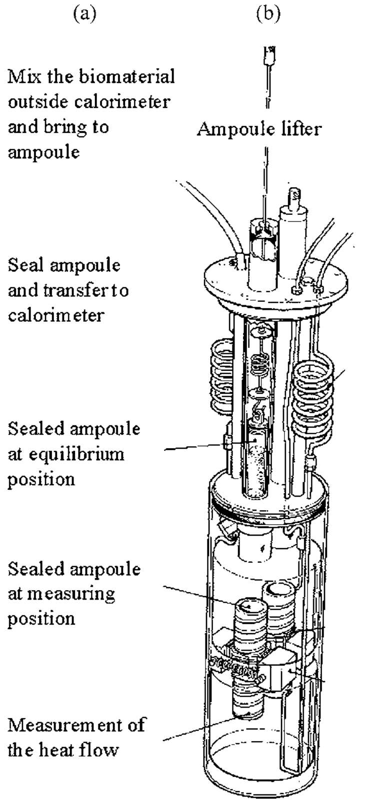


Fig. 2. Flow-chart for the thermometric monitoring of setting biomaterials: (a) procedures for preparing the dental adhesives; (b) experimental set-up of the TAM.

The water-vapour adsorption isotherms were determined by the so-called isopiestic method. Amounts of approximately 0.15 g of the dental adhesive was carefully prepared as described above. Then small tips cut from the lower end of eppendorf tubes were immediately filled with the biomaterial and quickly transferred to small containers with pre-set and constant relative humidity (RH) (Fig. 3). The humidity in the containers (climate chambers) was maintained with different salt solutions [19]. The samples were left inside the climate chambers for different periods of time. After the time elapsed, the specimen were taken from the containers and the amount of water adsorbed or released from the sample was determined gravimetrically. The differences in weight ΔW were calculated by

$$\Delta W = \frac{W_\mathrm{i} - W_\mathrm{e}}{W_\mathrm{i}} \times 100 \qquad (1)$$

where W_i is the initial weight of the specimen and W_e the weight of the sample after the time elapsed. Thus, positive values of ΔW expresses the evaporation of water molecules from the sample and negative values indicates the condensation of water at the specimen.

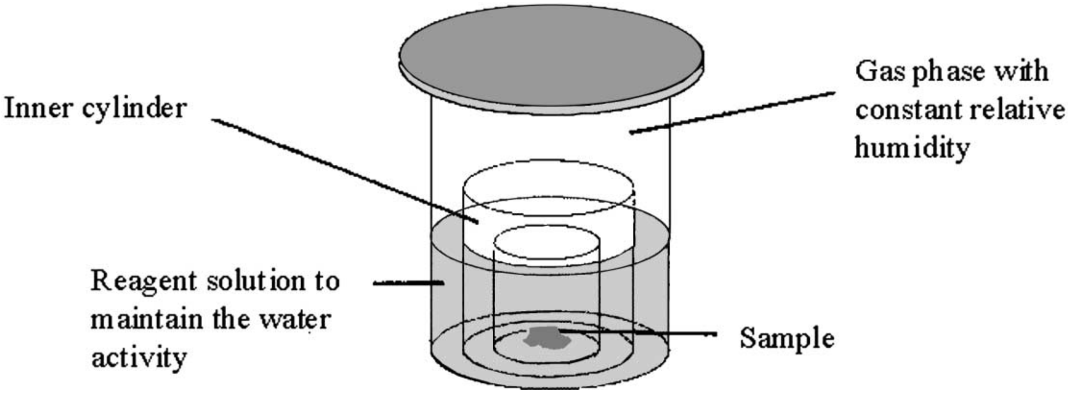


Fig. 3. Schematically set-up of the climate chambers for determining the water-vapour adsorption/desorption (isopiestic measurement).

3. Results

3.1. Heat flow-rate curves

The heat released from the different samples was continuously recorded for the early stage of the setting process. The results of our experiments are depicted in Fig. 4a–d in form of heat flow-rate versus time. The measured heat is extremely large for samples made from standard GIC (Fig. 4a). In the case of the RMGIC the heat evolved is distinctly smaller (Fig. 4b). For the samples of the composite adhesive (Fig. 4a) small exothermic signals were detected by the calorimeter.

To follow up the heat release over longer periods of time we increased the sensitivity of the TAM by the factor of 100. From Fig. 4c–d it can be seen that the ranking of the different biomaterials remains the same for the long term setting reaction, i.e. the heat release is the largest for GIC (Fig. 4c) and the lowest for the compomer material (Fig. 4d). The RMGIC samples (Fig. 4d) exhibit a somewhat intermediate heat flow-rate. Even after 3 days the GIC released noticeable amounts of heat (Fig. 4c), whereas the pure polymer sample is almost at the base line of the TAM (Fig. 4d). Again the resin modified GIC exhibits intermediate values in the $P = f(t)$ curves.

3.2. Water-vapour adsorption

The proceeding of the setting reaction of the different biomaterials was further analysed by measuring the release or uptake of water at constant RH (Table 1). Typical results of this procedure are graphically given in Fig. 5a–c. The measurements were performed at 0, 84 and 100% RH. These three values were chosen to simulate the different environments during the application of the biomaterials for the fixation of orthodontic attachments. First the storage over saturated KBr solution (84% RH) simulates the average moisture during dental treatment and fixation of the orthodontic attachment, whereas moisture adjustment by P_2O_5 (0% RH) and water (100% RH) corresponds to the extreme values of the RH which may occur upon handling. The results of the isopiestic measurements for specimen of the biomaterials stored over phosphorous pentoxide for time intervals of 10, 20 and 30 min (Fig. 5a) reveal that nearly 80% of the total weight of the GIC samples amounts to mobile water that can be extracted from the specimen by phosphorous pentoxide. It means that shortly after mixing of the components this biomaterial is extremely sensitive to drying and cracking. On the other hand, the composite material based on polymethacrylate did not release significant amounts of water. The polymethacrylate reference is practically inert to drying and cracking.

Table 1
Average change in weight of specimen (Eq. (1)) and enamel bond strength of dental materials

RH (%)	Dental material (wt.%) (Eq. (1))			Enamel bond strength (MPa)
	GIC	RMGIC	Composite	
0	82	26	0.05	3–12
84	17	7	0.08	6–20
100	3.5	−15	−1.4	20–28

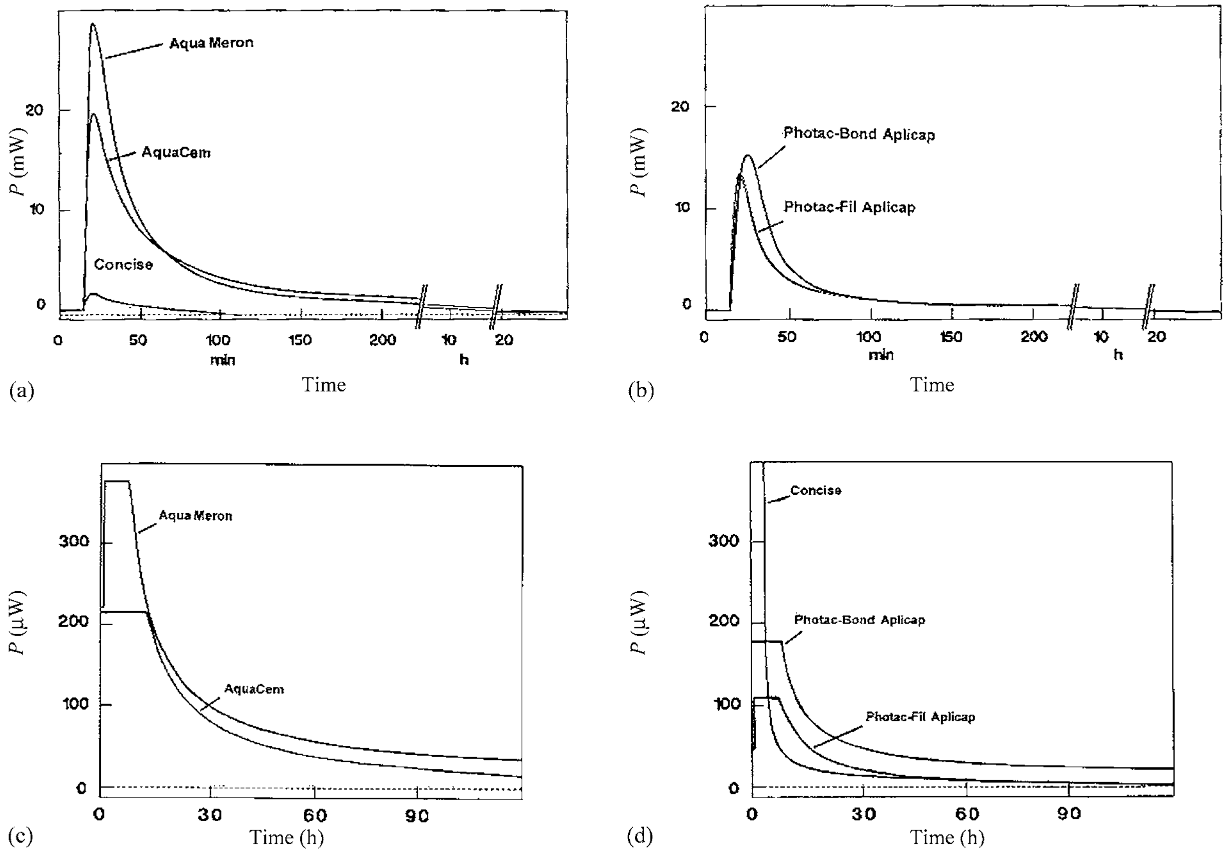


Fig. 4. (a) Heat flow-rate P vs. time for: (a) conventional GICs (AquaMeron, AquaCem) and the composite adhesive (Concise) in the early state of the setting reaction; (b) RMGICs (Photac-Bond Aplicap, Photac-Fil Aplicap) in the early state of the setting reaction; (c) conventional GICs (AquaMeron, AquaCem) over longer reaction times and increased sensitivity of the TAM; (d) composite adhesive (Concise) and RMGICs (Photac-Bond Aplicap, Photac-Fil Aplicap) over longer reaction times and increased sensitivity of the TAM.

The weight loss for the RMGIC is distinctly lower compared to the GIC material. The GIC releases about 25% of its total weight and in this respect it fits nicely between GIC and composite material.

The results from measurements at 84% RH, which is similar to the moisture content in the intra-oral environment during dental treatment are presented in Fig. 5b. The reference specimen made from composite samples is practically inert in this environment, whereas the RMGIC material is able to release approximately 7% of its own weight. In this climate chamber the GIC samples loses more than 15% of its weight, which is double of the amount determined for the RMGIC material.

Even when the atmosphere of the climate chamber was saturated with water (i.e. 100% RH) the GIC specimen release some of its water (Fig. 5c). Again the composite material based on polymethacrylate is almost inert, but the RMGIC apparently gains weight, which is indicative for some capillary condensation of water molecules and the formation of very small water droplets at the surface of the specimens.

4. Discussion

Even without further analysing the thermometric results we think that the heat curves recorded so far can nicely discriminate between the different materials. The form of the curves is indicative for the complex interference of several reactions involved in the hardening of GIC and the resin modified

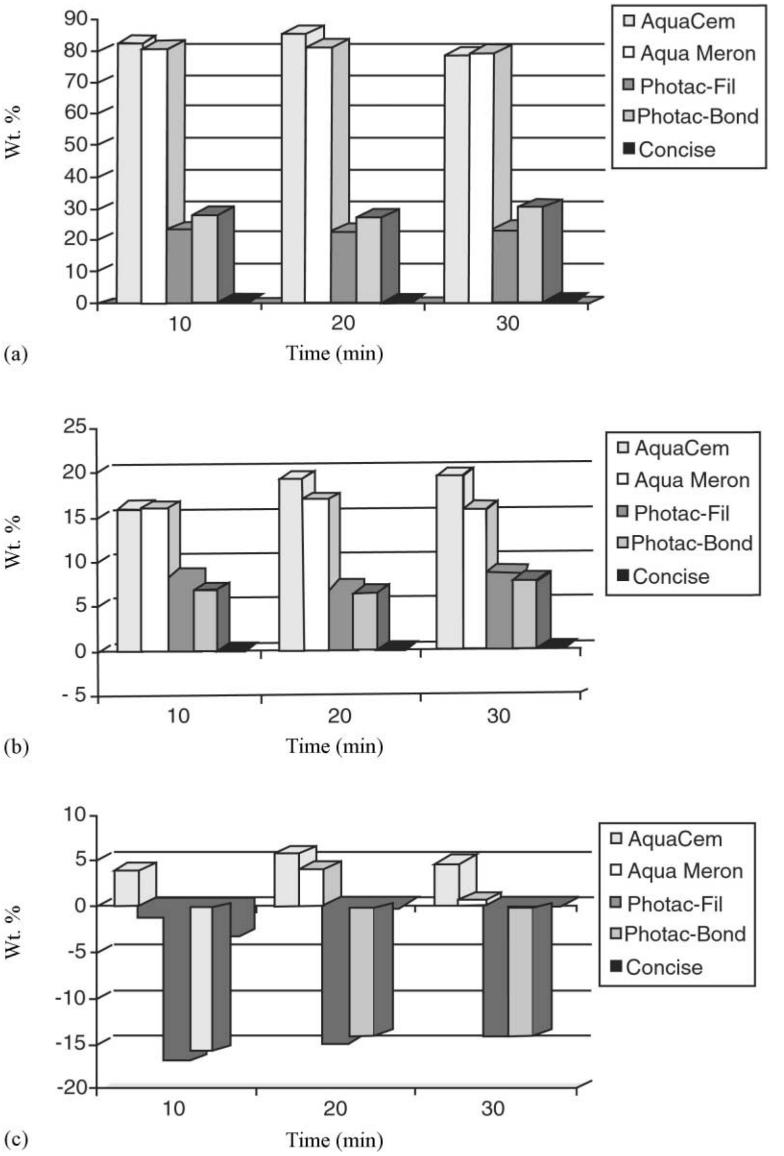


Fig. 5. Results from isopiestic measurements at different time after mixing the components at RH: (a) 0%; (b) 84%; (c) 100%.

material. Despite of the exact knowledge of the molecular mechanisms involved we can deduce for practical application of the three classes of materials that the RMGIC is a good compromise in respect to the reaction-rate and the heat evolved during the setting reaction of the biomaterial.

To analyse the mechanism of hardening of the dental adhesives it is essential to focus the attention to the composition of the different biomaterials. Table 2 shows the main ingredients of GIC, RMGIC and composite materials. Due to the fact that the different materials generally have a ionomeric character, one often uses the so-called continuum diagram, in which the direction of the arrow indicates a decreasing ionomeric (increasing resinous) character of the material under discussion [20].

In principle the hardening mechanism of all GIC is based on an acid–base reaction characteristic of dental

Table 2
Typical composition of the different biomaterials used in this study[a]

GIC	RMGIC	Composite
Ion-leachable glass	Ion-leachable glass	Non-reactive glass
–	Inert fillers	Inert fillers
Polyacid	Polymerisable acid	–
Water	Water	–
–	Polymerisable resins	Polymerisable resins

Ionomeric character of the material decreases

⟶

Resinous character of the material increases

[a] The direction of the arrow indicates increasing amounts of radical polymerisation and decreased setting by acid–base reaction, respectively.

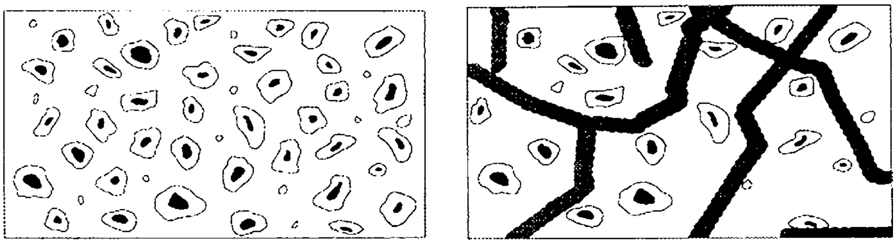
cements [11,12,20]. A hydrous polycarboxylic acid solution reacts with an ion-leachable calcium–aluminium–fluor–silicate glass, forming a hydrogel matrix, in which silicate glass particles are firmly imbedded after final hardening of the cement via chemical bonds. In the initial phase of GIC setting, Ca^{2+} and Al^{3+} ions are released by the reaction of acids with the silicate glass. The Ca^{2+} concentration available in the polyelectrolyte matrix increases faster than the Al^{3+} concentration and leads within a few minutes to a gelation of the matrix by combining the polyacrylic acid molecules via calcium bridge bonds. The calcium polycarboxylate gel is sensitive to moisture and changes after several hours into a stable, water insoluble Ca–Al–polyacrylate gel through the additional deposition of Al^{3+} ions. The final maturation and hydration processes of the cement can require up to several months.

The composite material used here behave quite different. The material is formed by the polymerisation of bisphenol-A–glycidyldimethacrylate (Bis–GMA) and different methacrylates in the presence of 70% inorganic silica filler particles. The hardening reaction of the composite material is very fast and this can be readily seen in the thermometric experiments. The magnitude and duration of the exothermic polymerisation of the composite is low compared to the heat released by the GICs and RMGICs.

The main limitation of biomaterials based on GICs are their weak mechanical properties and the lack of strength in the early states of the hardening process. They should not be subjected to undue masticatory load unless they are well-supported by surrounding tooth structure. There are on the other hand, some successful ways to modify the organic matrix of GICs. Modification can be achieved by simply adding hydrophilic monomers to the GIC or by incorporating readily polymerising polyalkenoic acid oligomers (macromers). The resulting group of dental materials is well-established as RMGICs. RMGIC materials have a dual-curing mechanism involving the acid–base reaction of the polyacid with the glass as well as the radical induced polymerisation reaction of the organic matrix [11,21]. A network of polyacrylic gel and polymeric chains is generated as the final product (Fig. 6).

There is some more difference between composite adhesives and materials based on GICs which is worth to be mentioned here. Water is an essential component of the GICs and the RMGICs. During the setting process water serves as a reaction agent. After hardening it stabilises the cement structure by hydration of the matrix.

From the isopiestic measurements it is obvious that the composite material has the lowest degree of hydration and forms relatively hydrophobic surfaces. On the other hand, the surface of the GICs is hydrophilic and the



(a) (b)

Fig. 6. Schematically sketch of the structure of the: (a) hardened conventional GIC; (b) dual-network of polyacrylic gel and polymeric chains of the RMGIC.

GIC material itself is highly hydrated. It forms a hydrogel upon setting and due to the high degree of hydration, hydrogels generally have low mechanical strength when compared to composite materials (cf. Table 1). In this respect RMGICs exhibit similar behaviour like hydrogels [20]. But the somewhat lower bonding strength of the RMGICs is truly balanced by its better biocompatibility. In contrast to the well-known enamel etching with phosphoric acid, which is necessary for the microretention of the composite adhesive, GICs adhere to the tooth surface by means of chemical adhesive forces [13,14,22]. By using RMGICs sufficient binding between the orthodontic attachment and the dental enamel is achieved without surface etching of the enamel. Thus, the so-called chemical interaction between dental enamel and RMGIC (like GIC) can minimise the loss in dental enamel.

The nature of the chemical adhesion of GIC and RMGIC to tooth surfaces has been studied with different kinds of carboxylic and polyacrylic acid using hydroxyapatite and polished or ground enamel as a model system [13,22,23,24] and evidence of the chemical binding has been reported recently [25]. Binding is achieved by carboxylate groups penetrating the apatite matrix and displacing calcium and phosphate ions. In recent studies we have analysed the topography of conditioned and untreated enamel surfaces by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) [13] and by atomic force microscopy (AFM) [26] and Fourier transform infrared (FT-IR) spectroscopy [20]. These analysis seems to be essential for the interpretation of the bonding between the dental enamel and the biomaterial layer. But nevertheless the mechanism of adhesion of restorative and sealing material to the tooth surface is still under conflicting discussion.

5. Summary and conclusions

We have measured the water uptake and heat evolution during the setting process of GICs, RMGICs and polymer based dental material. We deduced from thermometry and water-vapour adsorption experiments that the RMGIC is a fine combination of material properties. The RMGIC material has a much faster curing-rate when compared to the GIC. It is readily wetted like the GICs but is not so much sensitive towards dehydration. Moreover, the RMGICs can be used for bracket fixation without etching the dental enamel by phosphoric acid. Thus, we may conclude that the RMGIC material is the most flexible one for the fixation of orthodontic attachments.

References

[1] M.G. Buonocore, J. Dent. Res. 34 (1955) 849.

[2] G.V. Newman, Am. J. Orthodontics 51 (1965) 901.

[3] P. Diedrich, Praxis der Zahnheilkunde 12 (1992) 291.

[4] A. Thylstrup, G. Fejerskov, Textbook of Clinical Cariology, 2nd Edition, Munksgaard, Copenhagen, 1994.

[5] R.G. Craig, Restorative Dental Materials, 10th Edition, Mosby, St. Louis, 1997.

[6] T. Lie, Arch. Oral. Biol. 20 (1975) 739.

[7] G. Embery, T.G. Heaney, J.B. Stanbury, Arch. Oral. Biol. 31 (1986) 623.

[8] M.A. Vacca Smith, W.H. Bowen, Arch. Oral. Biol. 45 (2000) 277.

[9] A.D. Wilson, B.E. Kent, J. Dent. Res. 49 (1970) 7.

[10] A.D. Wilson, B.E. Kent, J. Dent. Res. 49 (1970) 21.

[11] A.D. Wilson, B.E. Kent, J. Appl. Chem. Biotech. 21 (1971) 313.

[12] A.D. Wilson, J.W. McLean, Glass-Ionomer Cement, Quintessence, Chicago, 1988.

[13] M. Es-Souni, R. Zimehl, H. Fischer-Brandies, Coll. Polym. Sci. 277 (1999) 382.

[14] R. Zimehl, M. Hannig, Progr. Coll. Polym. Sci. 117 (2001).

[15] H. Fischer-Brandies, G. Kluge, J. Theusner, K. Häusler, Deutsche Zahn-, Mund- und Kieferheilkunde 79 (1991) 349.

[16] V. Tsanidis, T. Koulouridis, J. Dent. Res. 71 (1992) 7.

[17] Instruction Manual, 2277 Thermal Activity Monitor, Thermometric AB, spjutvägen 5A, S-175 61 Järfälla, Sweden.

[18] Thermometric DIGITAM 2 Software Package (Version 2.0), Thermometric AB, Spjutvägen 5 A, S-175 61 Järfälla, Sweden.

[19] CRC Handbook of Chemistry and Physics, 55th Edition, CRC Press, Cleveland, 1974.

[20] R. Zimehl, M. Hannig, Coll. Surf. A 163 (2000) 55.

[21] D.C. Smith, J. Am. Dent. Assoc. 120 (1990) 20.

[22] A.D. Wilson, H.J. Prosser, D.M. Powis, J. Dent. Res. 62 (1983) 590.

[23] M. Hannig, Eur. J. Oral. Sci. 105 (1997) 422.

[24] H. Fischer-Brandies, R. Scherer, J. Theusner, K. Häusler, Fortschr. Kieferorthop. 53 (1992) 131.

[25] Y. Yoshida, B. van Meerbeek, Y. Nakayama, J. Snauwaert, L. Hellemans, P. Lambrechts, G. Vanherle, K. Wakasa, J. Dent. Res. 79 (2000) 709.

[26] M. Hannig, S. Herzog, S.F. Willigeroth, R. Zimehl, Coll. Polym. Sci. 279 (2001) 479.