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Characterization of the kinetic behavior of resin modified Glass-ionomer cements by DSC, TMA and ultrasonic wave propagation

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In this study the isothermal kinetic behavior of two resin modified glass ionomer cements (RMGIC) and a dental composite have been compared by differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). The simultaneous evolution of the multiple reactions occurring in RMGIC has been analyzed not only by DSC and TMA but also by ultrasonic wave propagation using the pulse-echo technique. The propagation of ultrasonic waves, acting as a dynamic mechanical deformation at high frequencies, is proportional to the longitudinal bulk moduli of the material and may be used to measure the changes of mechanical properties induced by a chemical reaction as occurs in RMGIC. TMA and ultrasonic analysis have been used to monitor the acid-base reaction of RMGIC in dark conditions. Moreover an RMGIC presenting a double reactive mechanism in dark conditions, a thermally activated radical polymerization and an acid-base reaction are studied using these experimental techniques. Finally DSC and TMA results obtained during photopolymerization of an RMGIC and of a dental composite have been compared.

1. Introduction

Dental amalgam has traditionally been employed as a material for cavity filling, but the use of this material is controversial (aesthetic problems, eventual toxicity etc). For this reason glass ionomer cements (GIC) and dental composites were introduced for restorative purposes [1–3]. More recently a new generation of glass ionomer materials, called RMGIC (resin modified glass ionomer cements), in which visible light-curing of double bonds is coupled with the polyacid matrix of conventional glass ionomer, has been developed. The setting reactions of these materials include a radical chain polymerization and an acid-base cross-linking reaction. The polymerization can be produced either by a chemical mechanism, with a thermal activated initiator, either by a photochemical mechanism, with a photoinitiator activated by visible light, (usually in the wavelength range 400–500 nm), or by the simultaneous presence of both initiators. The rate of the acid-base reaction and the final strength of glass ionomer cements depends on a number of factors such as molecular weight and composition of the polyacid matrix, concentration of acid solution and glass powder/liquid ratio. The dual setting system is expected to enhance the physical and mechanical properties of the glass ionomer, in particular, the polymerization should avoid the GICs hydrolytic decomposition by weak acids, which cause dissociation of the coordination bonds of the polyacid matrix with the cations released from the glass phase [4–7]. While the cure behavior of dental composites can be easily analyzed [8–10], being characterized by a single mechanism, the setting kinetics of RMGIC are not easily studied for the simultaneous occurrence of two chemical reactions. A further complication arises when the polymerization reaction in RMGIC is not only activated by light exposure but also by a thermal initiation system.

In this study the isothermal kinetic behavior of two RMGICs and a dental composite is compared applying three different experimental techniques: differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and ultrasonic wave propagation. The setting behavior of RMGIC and dental composites is traditionally studied using infra-red spectroscopy and DSC. In particular DSC, already applied in the past to the study of photopolymerization [11–18] allows the direct determination of the rate of reaction assuming that the heat produced by the polymerization is proportional to

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the number of monomer units reacted. Different types of dilatometers were also applied to the measurements of the polymerization shrinkage mainly for comparison of different commercial composites [10, 19–21]. Dental composites, presenting an initial high viscosity and good dimensional stability, are suitable systems for polymerization shrinkage measurements by TMA. Furthermore the shrinkage kinetics, coupled with the measurements of the mechanical properties during cure, represent an input for theoretical calculations of the residual stresses in restorations.

The simultaneous evolution of the multiple reactions occurring in RMGIC is also analyzed by ultrasonic wave propagation. Although ultrasonic wave propagation is a well-known technique for non-destructive analysis, its application as a thermal analysis technique for measurements of dynamic mechanical properties of polymers is very limited. Only a few papers are available on the characterization of the reactive properties of thermosetting resins by ultrasonic wave propagation [22–25]. The speed of propagation of ultrasonic waves, acting as a dynamic mechanical deformation at high frequencies, is proportional to the longitudinal bulk moduli of the material [26] and may be used as a measure of the changes of mechanical properties induced by a chemical reaction as those occurring in RMGIC and dental composites.

2. Experimental

The materials studied are produced by 3M and are two modified glass ionomer cements and a dental composite: Vitrebond is a commercial modified glass ionomer cement used as liner under every type of restorative material. This liner is characterized by two reactive mechanisms: an acid-base cross-linking reaction between an ion-leachable glass and an aqueous polyacid and a polymerization activated by visible light. The product is made of a solid powder and a liquid solution mixed in the ratio 1.4 : 1 by weight, as suggested by the manufacturer. The composition of Vitrebond material is given in Table I along with the manufacturers' data. The exact ratio of components is unknown, however the typical composition may be found in literature (for example in [5]).

Vitremer is an RMGIC indicated for restorative applications. Vitremer is characterized by the same two reactive mechanisms of Vitrebond presenting, in addition, a double initiation mechanism for the methacrylates polymerization: a photo-initiator activated by visible light and a thermally activated initiator. Vitremer composition presents some differences compared with Vitrebond: the powder phase contains a thermal activated initiator while the liquid phase also contains other multifunctional methacrylic monomers besides to 2-hydroxy-ethyl-methacrylate (2-HEMA). The composition of the reactive liquid and a powder to liquid ratio of 2.5 : 1 by weight indicates that Vitremer is characterized by a higher final content of inorganic filler and by a more densely cross-linked matrix, leading to a stiffer and harder material compared with Vitrebond.

TABLE I Composition of the two components of Vitrebond

Powder	Liquid
Fluoro-alumino-silicate glass	Caphorquinone and co-initiator Acrylic-itaconic acid copolymer with pendant methacryloxy groups 2-Hydroxy-ethyl-methacrylate (HEMA) Water

Silux Plus is a dental composite activated by visible light. The nature of the composite matrix is not explicitly indicated by the supplier. However, as reported in the literature [27–30], dental composites are typically made of a silica-based filler and of a matrix containing an aromatic methacrylate, the Bisphenol A-diglycidyl-methacrylate (Bis-GMA), and low viscosity aliphatic methacrylates, such as Triethylen-glycol-dimethacrylate (TEGDMA) and ethyler-glycol-dimethacrylate (EGDMA).

The cure of all materials has been carried out using a dental photopolymerization source (DEI Clever Lamp) consisting of a halogen lamp (100 W) equipped with a system of optical filters that are capable of emitting only in the blue region, strongly reducing the radiative heat flow. The light source is provided of a light guide with a diameter of 8 mm. The photo-calorimetric analysis was carried out with a differential scanning calorimeter (DSC), Perkin-Elmer DSC 7, operating in air. In order to allow the irradiation of the sample the furnaces have been closed by quartz covers and the light guide of the lamp was placed in correspondence of the sample pan. The experiments have been performed at the same temperature and exposure powers on open pans containing 18–20 mg of material corresponding to a thickness of 0.24–0.28 mm. The incident power has been obtained comparing the lamp specturm (Fig. 1) with the power output measured at 436 ± 5 nm using a band pass filter. The output power as a function of the distance from the sample is reported in Fig. 2.

The TMA has been carried out with a Netzsch TMA 402 operating in air. TMA experiments are performed in dark conditions and under the exposure of the lamp light. In order to allow sample irradiation, the standard furnace was removed and a heating device, connected with a thermostatic bath, was fitted around the probe and the sample, as shown in Fig. 3. TMA experiments have been performed using samples of the same thickness to those used for the DSC tests. A thin film has been prepared placing the material between two glass covers. The TMA probe, loaded with 5 g, has been placed in contact with the upper glass plate while irradiation has been performed on the opposite side (Fig. 3). As reported by De Gee *et al.* [21] the adhesion between the sample and the glass covers must be prevented since it may lead to overestimated values of shrinkage. For this reason a mold release agent (Freekote) has been applied on both glass plates in contact with the sample. The output power as a function of the distance from the sample for the TMA configuration is also reported in Fig. 2. The curves of Fig. 2 have been used to set the same power output in DSC and TMA experiments.

The longitudinal velocity of ultrasonic waves has been measured during dark reaction of Vitrebond and

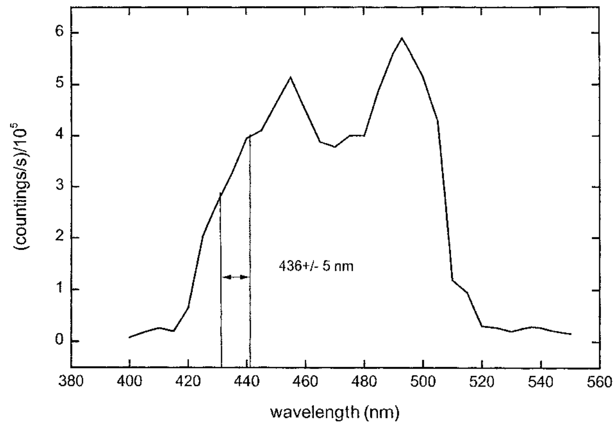

Figure 1 Power spectrum of the used lamp.

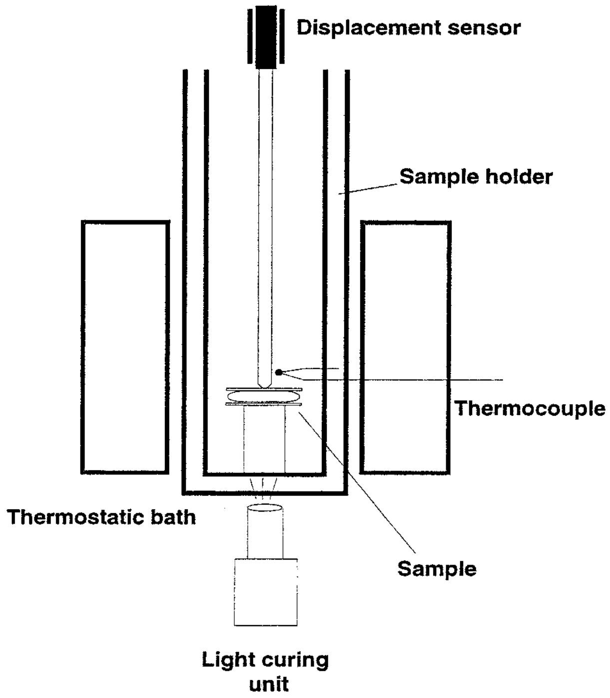

Figure 3 Sketch of the TMA apparatus as modified for photopolymerization measurements.

Vitremer by the pulse-echo technique at the frequencies of 10 Mhz using a Panametrics 560A1-ST system connected with an oscilloscope (Philips PM3323). The ultrasonic measurements have been performed in isothermal conditions by placing the resin sample, in the form of a thin film, at constant temperature (± 1 °C), between a buffer rod, at the opposite end of which the transducer is placed, and a heated plate. The same temperature conditions and sample thicknesses of the DSC and TMA experiments were used. Since the studied materials are activated by visible light, the samples have been kept in dark conditions during sample preparation and during the elapsing time before starting the measurements.

3. Results and discussion

The dark reaction of Vitrebond and Vitremer is analyzed by TMA and ultrasonic wave propagation. The effect of radical chain polymerization in Vitremer is clearly observed using TMA as shown in Fig. 4. The dimensional changes associated with the acid base reaction in Vitrebond are much lower than those observed for Vitremer, where a radical chain polymerization of multifunctional methacrylate monomers also occurs. Comparing the behavior of Vitrebond and Vitremer, it must be noted that the radical cross-linking process is significantly faster than the acid-base reaction. The linear contraction curve in Fig. 4 obtained on Vitremer reaches a plateau while the Vitrebond is still reducing its dimensions as a consequence of the acid-base reaction. This result indicates that an interaction between the two reactive mechanisms occurs in Vitremer when the double bonds have significantly reacted and a polymeric network has been formed. The rate of the acid-base reaction should be similar for the two materials or higher for Vitremer, being characterized by a higher content of glass powder. At long curing times, when the radical chain reaction in Vitremer is terminated, the acid-base cross-linking reaction should be observed by TMA. However, at long curing times, the slope of the shrinkage curve measured for Vitremer flattens while the Vitrebond sample is still contracting. The cross-linked methacrylic matrix developed in Vitremer is probably responsible for a reduced mobility of cations and in particular of the anions bound to the polymer network. Then, in these conditions the acid-base reaction is under the control of diffusion and its effects on contraction are not evident in the experimental time scale of Fig. 4.

During the dark reaction of Vitrebond, the velocity of

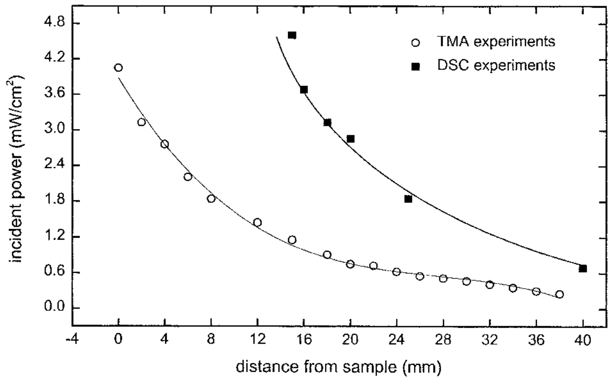

Figure 2 Output power as a function of the distance from the sample for the TMA and DSC experiments.

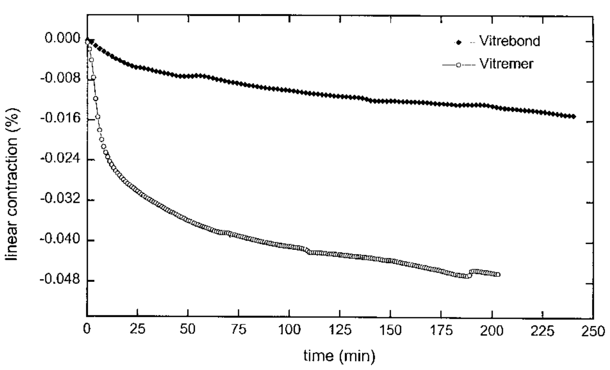

Figure 4 Results of a TMA experiment obtained in dark conditions for RMGIC Vitremer and Vitrebond.

ultrasonic waves is measured. The propagation of elastic waves at high frequency, as in the ultrasonic range, correspond to a dynamic mechanical deformation imposed on the material. This deformation produces a displacement around the equilibrium position of atoms and chain segments in the nm range, so the information that can be obtained from the ultrasonic measurements is related to small-scale mobility of short segments between entanglements and cross-linking sites. On the other hand, the deformation rate is very high since the typical frequencies of analysis range from hundreds of KHz to tens of MHz. When an alternating time-dependent deformation at the ultrasonic frequencies is applied to a material, the velocity of propagation of elastic waves (called ultrasonic or acoustic velocity) can be measured. The measurements of these quantities can be carried out only if the samples are sufficiently larger than the wavelength, typically higher than 0.15 mm for a polymer at a frequency of 10 Mhz, and sufficiently small to allow the detection of the wave traveling from the ultrasonic transducer to the receiver [26, 31, 32]. The longitudinal velocity, V_L in the pulse-echo mode, is defined as the ratio between twice the sample thickness, d and time of flight, t, of the ultrasonic wave through the sample

$$V_L = 2d/t \tag{1}$$

The propagation of longitudinal elastic waves is easily observed in polymers as well as in reactive mixtures of monomers. When the sample dimension normal to the direction of propagation of the acoustic waves is large compared with respect to the wavelength, the wave propagation is governed by the bulk longitudinal modulus L, related to the bulk (K) and shear (G) moduli by [26]

$$L = K + 4/3G \tag{2}$$

For low damping solids where the attenuation of the waves across the material may be neglected and the bulk longitudinal modulus can be calculated as a function of the density p and of V_L as $L = \rho V_L^2$. Therefore, the changes of V_L can be related to changes of mechanical properties. In particular, L corresponds to the stiffness of a system that is deformed changing its dimensions in one direction while in the other two directions the dimensions are constrained to be constant, as occurs in samples where two dimensions are much larger than the third [26].

In order to compare the TMA and ultrasonic data a normalization of the data is performed. Then, the degree of reaction obtained by TMA α_{TMA} is obtained as a function of the maximum shrinkage observed at the end of the experiment $(\Delta L_{\max})$

$$\alpha_{\mathrm{TMA}} = \Delta\mathrm{L}/\Delta L_{\max} \tag{3}$$

The degree of reaction obtained from ultrasonic data (α_{US}) is calculated as a function of the initial and final ultrasonic velocities, V_{Lo}, V_{lmax}

$$\alpha_{US} = (V_L - V_{Lo})/(V_{\max} - V_{Lo}) \tag{4}$$

In Fig. 5 the comparison of α_{TMA} and α_{us}, obtained for Vitrebond in dark conditions is presented. The two curves are very close indicating that the shrinkage observed during the acid-base reaction occurring in dark conditions in Vitrebond is also accompanied by a stiffening of the material. The experimental setup adopted for TMA and ultrasonic analysis prevented the evaporation of the volatiles during the acid-base reaction in Vitremer and Vitrebond. The study of the dark reaction of RMGIC by DSC is made complex as a consequence of the evaporation of water and HEMA, not negligible in the DSC sample pan in a time scale of about 250 min. On the other hand, the photoactivated radical polymerization of RMGIC may be studied by DSC since the polymerization occurs in no more than 200 s and in this time interval the effects of volatiles evaporation is negligible.

A typical DSC thermogram obtained at 25 °C on Vitrebond is reported in Fig. 6. When the lamp is turned on, an exothermic peak is immediately detected. The peak is produced by the sum of two contributes: the exothermic effect due to the cure reaction and the radiative heat flow of the lamp. These two contributions are easily distinguished, as shown in Fig. 6, comparing the heat flow measured on a further exposure of the already cured sample. The measured signal goes through a maximum and then returns to the baseline value during continuous irradiation of the sample.

The DSC measurements are commonly used for determination of the advancement of the polymerization assuming that the heat evolved during reaction is proportional to the overall extent of reaction given by the fraction of reactive groups consumed. Following this approach the degree of reaction, α_{DSC}, is defined as

$$\alpha_{\mathrm{DSC}} = Q(t)/Q_{ref} \tag{5}$$

where $Q(t)$ is the partial heat of reaction developed during a DSC experiment measured from the baseline value and Q_{ref} represents a reference value. In this study Q_{ref} is assumed as the total heat of reaction measured integrating the peak area under the baseline. Therefore α_{DSC} is a normalized degree of reaction ranging from 0 to 1. If Q_{ref} is assumed as the maximum heat of reaction, an absolute value of α_{DSC} would be obtained [8].

The comparison of the degree of reaction measured by DSC and TMA during light activated polymerization of Vitrebond is reported in Fig. 7. The overall reaction time

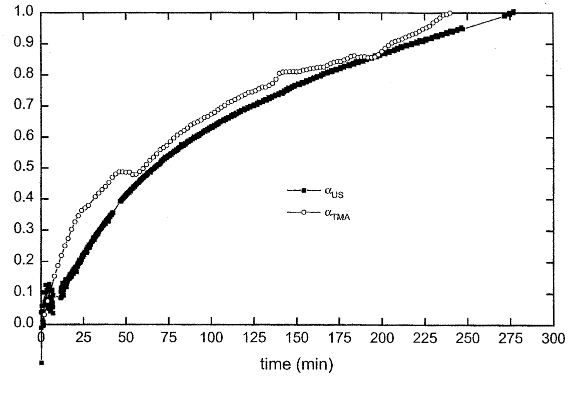

Figure 5 Comparison of α_{TMA} and α_{US}, obtained for Vitrebond in dark conditions.

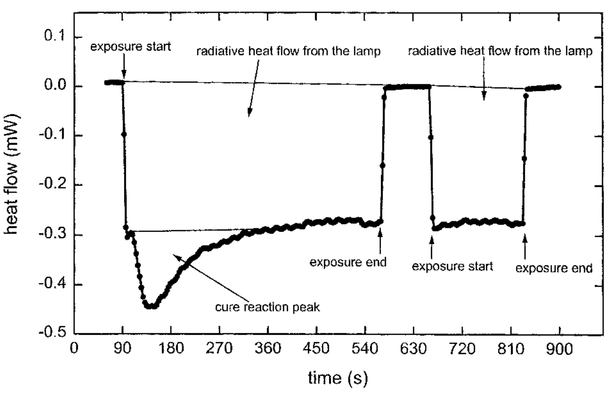

Figure 6 Typical DSC thermogram obtained at 25 °C on Vitrebond.

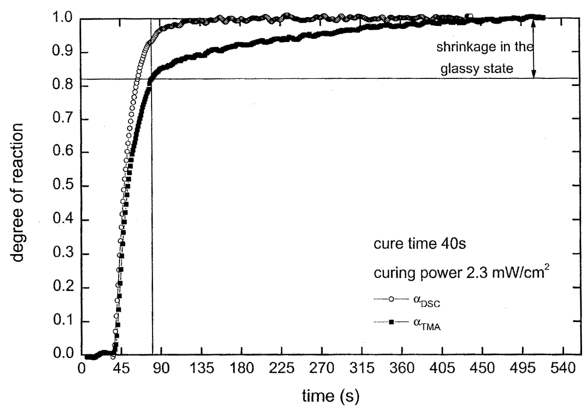

Figure 8 Evolution of the degree of reaction measured by DSC and TMA during light activated polymerization of Silux Plus.

is of the order of 100 s, much lower than that of the acid-base cross-linking reaction. Therefore, the effects of this reaction on the photoactivated polymerization may be neglected. As shown in Fig. 7, after a few seconds for the stabilization of the signals, the samples are irradiated and a sharp increase of α_{DSC} and α_{TMA} is observed. Before the lamp exposure is interrupted (after 40 s) the rate of reaction decreases and only a limited increse of the degree of reaction is detected at longer times in dark conditions. During the reaction the two curves follow the same path indicating a correspondence between the chemical conversion measured by DSC and the shrinkage observed by TMA. This correspondence is not observed during photopolymerization of a dental composite as shown in Fig. 8. In this figure, where the comparison between α_{DSC} and α_{TMA} obtained on Silux Plus is reported, a different behavior is clearly detected: a delay of the sample shrinkage occurs for a degree of reaction higher than about $\alpha = 0.3$. Moreover, after the interruption of the light exposure (40 s) the α_{DSC} curve levels in a few seconds while α_{TMA} continuously grows for about 300 s.

A delay between DSC and TMA degree of reaction was observed [33, 34] during photoactivated polymerization of acrylic resins. In fact, the volume shrinkage cannot keep up with the chemical reaction, at least after gelation when the resin becomes a viscoelastic solid. The viscoelastic behavior of the material leads to a delayed shrinkage with respect to the evolution of the chemical reaction as observed by DSC. Therefore, the rate of reaction acts as the driving force for the rate of volume change while the material response is governed by a retardation time, dependent on the cross-linked structure and hence on the degree of reaction. The shrinkage of a curing resin may be compared as a bulk creep recovery experiment in which the equilibrium volume, continuously changing, is uniquely determined by the value of the chemical conversion. After gelation, the rate of reaction is too high and the shrinkage of the material cannot keep up with the reaction

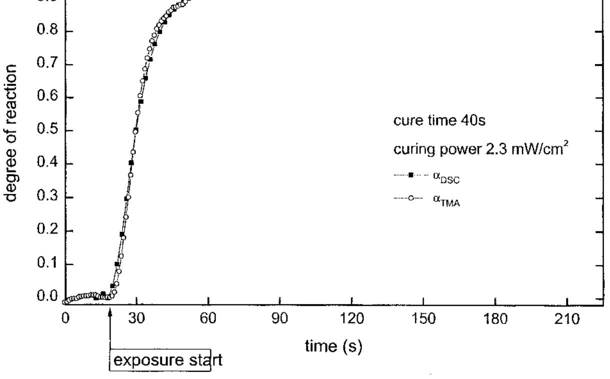

Figure 7 Evolution of the degree of reaction measured by DSC and TMA during light activated polymerization of Vitrebond.

In correspondence of the vitrification in the reaction, as measured by α_{DSC}, is terminated and the volume moves toward the equilibrium value, imposed by the value of α_{DSC}, in the glassy state. The observed delay between the TMA and DSC degree of raction may therefore be interpreted as the inablity of the rate of volume shrinkage to follow the rate of chemical conversion leading to an excess of free volume. In fact, as reported by Kloosterboer [33] the chemical reaction generates the free volume that is responsible of the diffusion of monomers and radicals. At the same time, the polymerization is the driving force for the volume shrinkage which follows with delay the chemical conversion on the basis of a sort of viscoelastic creep recovery response characterized by a time dependent bulk retardation time. The inability of the rate of volume shrinkage to follow the rate of chemical conversion leads to a non-equilibrium condition in which a degree of reaction calculated using volume shrinkage, α_{TMA}, is always lower than the equilibrium value imposed by the actual degree of reaction measured by DSC [10, 33, 34]. Finally, it must be noted that the delay of the α_{DSC} curve in Fig. 8, dependending on the viscoelastic response of the composite, indicates a reduced capability of relaxation of the shrinkage stresses arising during cure in a constrained geometry like a dental cavity.

The different reactive behavior shown by Vitrebond and Silux plus in Figs 7 and 8 may be explained considering that the photoreactive components of Vitrebond contain monofunctional hydrophilic methacrylates in an aqueous environment. Water, acting as a plasticizer for the growing polymer, prevents the vitrification allowing a fast contraction of the resin during cure. The coincidence of TMA and DSC curves occurring for Vitrebond indicates that the retardation time of the polymerizing resin is always low compared with the characteristic cure time. Therefore, for an RMGIC like Vitrebond, the relaxation of residual stresses, arising from shrinkage, should occur more rapidly than in a dental composite. This results from the more compliant nature of a liner, like Vitrebond, that plays an important role in the durability of a restoration. In fact, besides the adhesion properties a liner is also responsible for the relaxation of the stresses induced not only by its cross-linking but also transferred by the contraction of the filling materials (such as photo-activated composites).

4. Conclusions

In this study, the complex cure behavior of commerical resin modified glass ionomer cements and of a dental composite have been analyzed in isothermal conditions by DSC, TMA and ultrasonic wave propagation. TMA and DSC equipments have been appropriately adapted for light exposure of the sample during measurements. Isothermal TMA and DSC data and ultrasonic velocity have been processed in order to obtain the degree and the rate of reaction. TMA and ultrasonic analysis have been used to follow the acid-base reaction of RMGIC in dark conditions and the complex double reactive mechanism of Vitremer, where a thermal initiator is responsible of a radical polymerization occurring immediately after mixing.

DSC and TMA results obtained during photopolymerization of an RMGIC and a dental composite have been compared. The delay of the degree of reaction measured by TMA compared with that measured by DSC in a dental composite has been interpreted as the inability of the rate of volume shrinkage to follow the rate of chemical conversion, leading to a reactive behavior governed by the interaction between the photopolymerization process and a volume creep recovery process. The different behavior observed for the RMGIC has been explained taking into account that RMGIC, being plasticized by water, is characterized by lower retardation times.

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