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The study of a commercial dental resin by ^{1}H stray-field magnetic resonance imaging

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Abstract

A dentine/enamel resin containing methacrylate monomers, included in a new generation adhesive system, was used to evaluate the potentialities of recent nuclear magnetic resonance imaging (MRI) techniques to obtain spatially-resolved information on photo-polymerization reaction and subsequent polymerization shrinkage. ^{1}H stray-field (STRAFI)-MRI one-dimensional images (1D profiles) of visible-light cured resins were obtained in the presence of oxygen from the atmosphere, and the variation of magnetization with irradiation time was recorded for each resin slice. The polymerization shrinkage was obtained from 1D profiles. The spatial distribution of the unreacted methyl methacrylate groups was obtained from 3D STRAFI experiments. In particular, the thickness of the surface remaining unpolymerised was measured.

Keywords: Stray-field magnetic resonance imaging; Composite resin; Photo-polymerization

1. Introduction

Dimethacrylate networks are widely used as dentinal bonding agents [1,2]. The dentin–resin interface, produced by total-etch adhesive systems, like All-bond 2 (AB2), was observed using scanning electron microscopy and information on the bonding mechanism was obtained through the examination of the induced changes, for example, in dentine surfaces [3]. AB2 includes hydrophilic monomer primer solutions and an unfilled resin, and is used prior to inserting the final restoration material. According to the manufacturer, the unfilled resin contains 2,2-bis-4-(2-hydroxy-3-methacryloyl-oxypropoxy) phenyl propane (bis-GMA), as well as two other methacrylate monomers: 1,6-bis-(methacryloxy-2 ethoxy carbonylamino)-2,4,4-trimethylhexane (UDMA) and 2-hydroxyethyl methacrylate (HEMA). In addition, it is indicated that the formulation contains dihydroxyethyl *p*-toluidine (generally used as an activator in chemically activated reactions) and dimethylamine ethylmethacrylate (a reducing agent, currently used in conjunction with a photosensitizer in light activated reactions).

Upon polymerization, the free volume of the resin changes because the resin contracts towards the surface exposed to the light source. In vinyl polymerization, this inevitable contraction is related to the exchange of a double bond and a van der Waal's bond for two single covalent bonds. Polymerization shrinkage (PS) not only determines the durability of the material, due to the internal strain and stress produced, but also the ingress of fluids and ensuing infiltration of bacteria is facilitated. Resin contraction stresses within the resin may reach 7 MPa [4]. Accordingly, in order to avoid resin dentin gap formation, filling materials with shear bond strengths of 17–20 MPa may be required [5]. PS has been usually determined as total volumetric change from dilatometric or density measurements. More recently, disc-shaped specimens have also been used in order to obtain the shrinkage that occurs in a direction perpendicular to the sample surface [6]. However, this method assumes that the resin is placed between two glass plates and, consequently, the influence of oxygen is not observable. The role of oxygen in photochemical reactions is well known; oxygen is reactive towards excited molecules and free radicals [7]. In oral environment, the reaction takes place in the presence of oxygen and other fluids. This fact accounts, in part, for the existence of liquid monomers and unreacted groups, even after a long irradiation period, which determines the mechanical properties of the resin. Indeed, upon polymerization, dimethacrylate monomers undergo extensive cross-linking. However, the unsaturation in the

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final product may be considerable, ranging from 25 to 45%, which means that degrees of conversion in the range 55–75% may be achieved [8–10].

The dentin–enamel bonding resin, incorporated in the AB2 adhesive, was studied using ^{1}H stray-field magnetic resonance imaging (^{1}H STRAFI-MRI), which not only enables the observation of liquids and soft materials, but also allows to image hard materials, like crystalline polymers [11–13]. STRAFI-MRI uses a static magnetic field in conjunction with a static magnetic field gradient. Based on the use of this technique, we propose a novel method to measure the PS of resins, in the presence of any fluid, like water or saliva. Moreover, using this method, it is possible to map the distribution of mobile domains in the cured resin, related with non-polymerized methacrylate moieties.

2. Experimental

The AB2 dentin–enamel bonding resin, batch number 089227, was obtained from Bisco (Itasca, IL, USA) and used as received. An Optilux 401 (Demetron/Kerr, Danbury, CT, USA) was used as a visible (blue) light-activation unit (470 nm); the diameter of the light guide was 1 cm.

An MSL 300P spectrometer (Bruker Spectrospin GmbH, Karlsrhue, Germany), equipped with wideline and dedicated STRAFI probe-heads, was used for ^{1}H observation at 123 MHz. The static magnetic field gradient of 3750 G/cm, present outside the superconducting coil, was employed to select a slice of the material. To obtain one- to three-dimensional images (1D–3D), cylindrical glass vials (height 1.1 cm and internal diameter 1 cm) were filled with the liquid resin up to 0.5 cm height and the light source was placed at fixed distances from the top of the containers, as shown in Fig. 1 (at 0.5 or at 10 cm, in order to irradiate the sample with 400 or 1 mW/cm^2 light intensity, respectively). A plastic disc was used to obtain a reference signal, which is shown on the right side of Fig. 2, also the bottom of the vials. To record 1D images, the protons in the selected

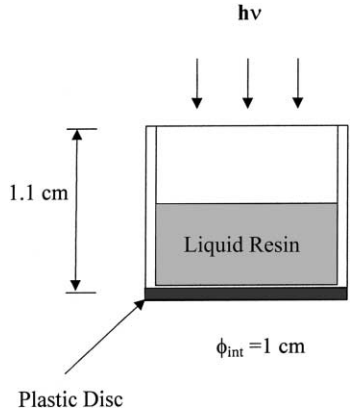

Fig. 1. Set up used for ^{1}H STRAFI-MRI observations of the visible light-curing reaction of the dentin–enamel bonding resin of AB2.

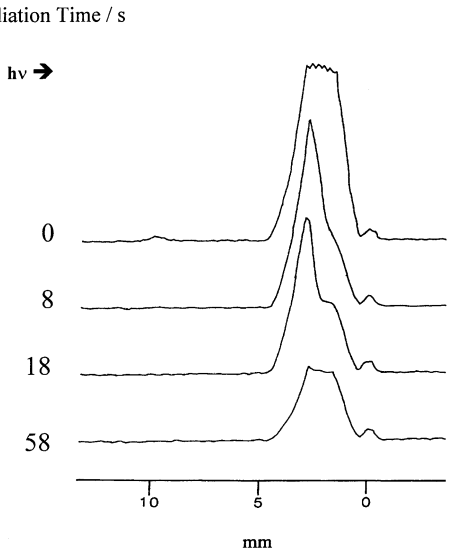

Fig. 2. STRAFI-MRI ^{1}H magnetization 1D projections of the dental resin, along the cylindrical axis of the container, obtained before light-irradiation of resin and after 8, 18 and 58 s light-curing periods using a light-source intensity of 1 mW/cm^2. The RF pulse duration was 10 μs and the corresponding slice thickness was ~54 μm. Other relevant parameters were: echo-time 15 μs and relaxation waiting period 6 s.

slice were submitted to a radio frequency (RF) pulse sequence (see Ref. [14] for details) and the magnetization was recorded as multiple spin-echo decay. After a relaxation waiting period, the sample was moved linearly (using a computer controlled step motor) and the magnetization of the next slice was acquired. Each data point in the profiles is the result of the summation of all echoes (typical 8) in each echo-train. This procedure was repeated until the first scan of the object was completed, then the sample was moved down to the initial position and the process was repeated until the selected number of scans was reached. The observation of 2D and 3D images required, respectively, one and two additional movements, which were performed along one and two different (perpendicular) rotational axes. Data were acquired at the probe-head temperature (~23°C).

3. Results and discussion

Fig. 2 shows the 1D ^{1}H-magnetization projections recorded from samples in cylindrical glass containers, with dimensions as described in Section 2, which were irradiated at 10 cm from the top and the intensity of the light-source was 1 mW/cm^2 (Fig. 1). The profiles were obtained along the cylindrical axis, also the magnetic field and the magnetic field gradient directions, before any light-irradiation of the liquid resin and after 8, 18 and 58 s light-curing time (eight echoes were acquired in each echo train). The linear resolution was about 54 μm, for the selected RF pulse duration of 10 μs. PS of the resin is clearly observed. In particular, the contraction along the cylindrical axis, following each light-curing period, was

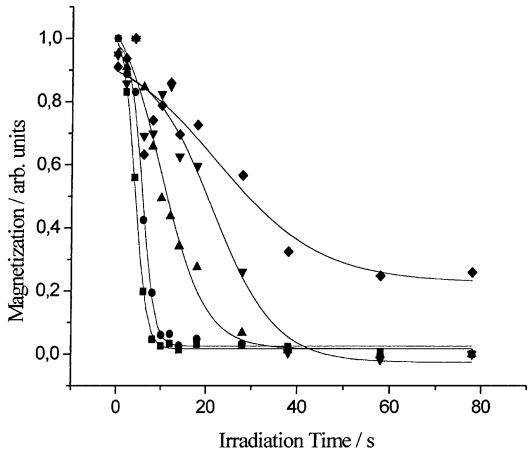

Fig. 3. Variation of STRAFI-MRI ^{1}H magnetization (in arbitrary units) with light-curing time, obtained from resin slices at the indicated distances from the bottom of the container. Light-source intensity: 1 mW/cm^2. Distance from the bottom of the container (mm): (■) 1.12, (●) 1.50, (▲) 2.00, (▼) 2.38, (◆) 3.13.

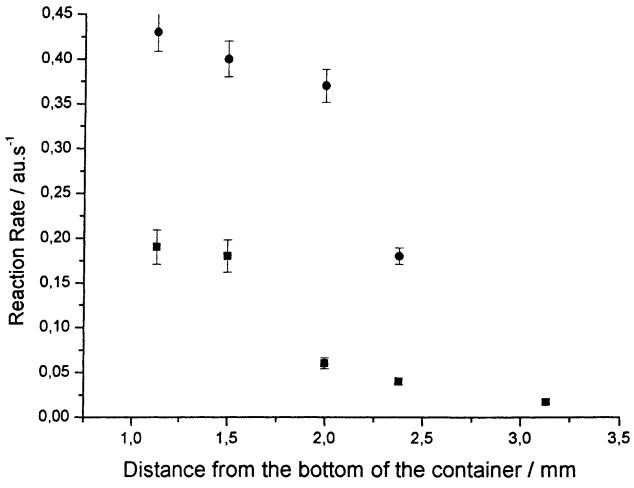

Fig. 5. Reaction rates of resin slices at the indicated distances from the bottom of the container, recorded for the following intensities of the light-source: 400 (●) and 1 mW/cm^2 (■). The rate is expressed in magnetization (arbitrary units) per second.

measured as the variation of the width at half-height of the corresponding profile, in comparison with the uncured resin profile. At the end of the irradiation periods the PS was about 10%. In all the profiles, the highest signal intensity was obtained from slices close to the resin surface, which was in contact with air.

Fig. 3 shows the variation of ^{1}H magnetization (M) with light-curing time, obtained from resin slices at specified distances from the bottom of the container. The distance of the light source from the resin surface was 10 cm and the intensity of the light source was 1 mW/cm^2. Sigmoidal (Boltzman) functions, $M = (M_1 - M_2)/[1 + e^{(t-t_0)/t_c}] + M_2$, were used to fit the experimental data, where M_1 and M_2 are the magnetizations recorded before and after the irradiation period, respectively, and t_c is the reaction time constant. The reaction rates, $M' = d[M]/dt$, were obtained as the derivative at the irradiation time t_0, at which the magnetization reaches half the initial value: $M' = (M_2 - M_1)/4t_c$. Fig. 4 shows plots of t_0 as a function of the distance of the slice from the bottom of the container, obtained for 400 and 1 mW/cm^2 light-source intensity, respectively. It is clearly shown that, at higher intensity of the radiation source, t_0 is nearly constant for all the observed slices at a distance from the bottom of the container equal to or less than 2.4 mm: 1.85 ± 0.15 s. Fig. 5 shows the reaction rates obtained for resin slices at different distances, as a function of the light-source intensity: 400 and 1 mW/cm^2, respectively.

In order to map the distribution of unreacted methacrylate moieties, 3D STRAFI images were obtained from cylindrical samples (Fig. 1). 1D images were first obtained and the corresponding 2D image was reconstructed by back-projection. Subsequently, 3D images were obtained from back-projection reconstruction of 2D images. Fig. 6 shows two groups of four consecutive slices, selected along the *XY* plane (perpendicular to the cylindrical axis, *Z*, Fig. 1) and along the *XZ* plane, respectively, obtained from the resin cured over 58 s. The more mobile domains are reproduced in white. A resolution of about 100 μm was achieved in all

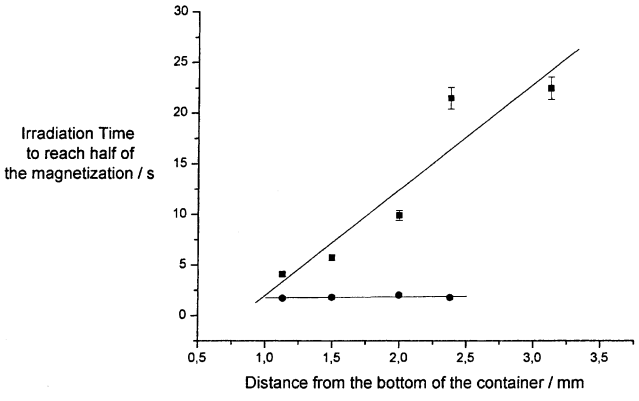

Fig. 4. Influence of the intensity of the light source (mW/cm^2) expressed as the irradiation time (s) needed to reach half of the magnetization (arbitrary units) versus the distance from the bottom of the container (mm): (■) <1, (●) 400.

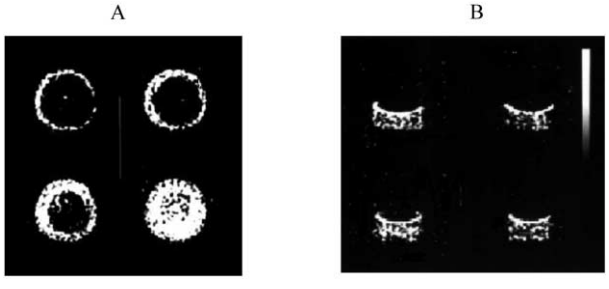

Fig. 6. Four consecutive slices obtained along the *XY* plane (A) and along the *XZ* plane (B), respectively. The first slice shown is: (A) the surface slice and (B) the middle slice. The more mobile domains are reproduced in white. A resolution of about 100 μm was achieved in all directions, with a 128 × 128 × 128 voxel.

directions, with a $128 \times 128 \times 128$ voxel. The contrast attained is mainly a T_2 contrast because only eight echoes in each echo-train were recorded. The spatial distribution of unreacted groups is observed (white); in particular, a surface layer, with a thickness of about 500 μm, is clearly detected.

NMR signals acquired using STRAFI-MRI contain the following contributions: magnetization from protons in mobile molecules, like free monomers (with long spin–spin, T_2, and spin–lattice, T_1, relaxation times) and magnetization from protons in rigid molecules, like cured AB2 resin (with short T_2 and long T_1), not observable by conventional MRI methods. Consequently, it is possible to obtain STRAFI images containing data from all the protons in the sample or to visualize only the spatial distribution of free monomers and non-polymerized moieties, using a relaxation weighted acquisition [13]. In MRI, the linear resolution Δx, that is, the thickness of the excited slice depends mainly on $\sqrt{3}\pi/(t_p \gamma_H G_Z)$, where t_p is the RF pulse duration that is related to the frequency range to be excited, γ_H is the proton magnetogyric ratio and G_Z is the magnetic field gradient along the Z axis, also the axis of the static magnetic field [12]. For example, selecting a pulse duration of 10 μs and an applied G_Z of 37.5 T/m, Δx would be about 54 μm. These were the conditions selected to obtain the data shown in Fig. 2, which allowed the determination of PS.

The spatial-dependence of the photo-polymerization kinetics is also presented here. The inhibitor effect of oxygen is shown: the free monomer concentrates on top of the cured resin, which is in contact with air, showing that the polymerization reaction was inhibited within a surface layer of about 500 μm. Also, it may be observed that the depth of cure was higher than the thickness of resin, even for very low intensity values. Photo-calorimetric measurements have already shown that the reaction of resin monomers follows first-order kinetics in many visible-light cured systems [15]. More recently, infrared spectroscopy measurements were reported on composite resin conversion kinetics, during exposure with stepped or continuous light curing [16]. The degree of conversion and the maximum rate of reaction were monitored and stepped intensity curing was shown to produce significantly lower conversion rates at the surface and at 1 mm depths.

PS was also obtained, which was higher than the values found in dental literature, measured in the absence of oxygen. Equilibrium shrinkage magnitudes of 7.9% were obtained for unfilled resins [6]. Recently, it was found that the bis-GMA-based resins exhibited lower shrinkage when bis-GMA was mixed with monomethacrylates rather than with conventional glycol dimethacrylates [17]. In general, it is considered that light-curing resin composite shrinks towards the light source. However, it was recently shown that, in certain conditions, and depending on the thickness of the material, the shrinkage direction could be different [18]. Other aspects on light-cured resin shrinkage, like the possibility of reducing the rate of initial shrinkage and the subsequent clinical benefits, have been investigated [19]. These and other aspects of resin shrinkage are now under study, using STRAFI-MRI, which will be extended to the observation of resins applied in human tooth cavities. In addition, because magnetic susceptibility inhomogeneities do not impose any limitation to STRAFI-MRI observations (after the Zeeman term, the strong magnetic field gradient is the major contribution to the spin system Hamiltonian), PS dependence on inorganic resin filler concentration will be evaluated.

4. Conclusion

In the present study, spatially resolved information on the kinetics of photo-polymerization, PS and distribution of unreacted methacrylate groups were obtained. Moreover, the thickness of the non-polymerized resin surface layer was measured. PS is an important clinical drawback of unfilled resins. Also, in oral environment, the presence of oxygen strongly influences the spatially resolved kinetics of the reaction. ^{1}H STRAFI-MRI proved to be a suitable technique for the elucidation of such aspects, which are relevant for the preparation of adhesive formulations with improved properties. It was also demonstrated that by using STRAFI-MRI, it is possible to follow the kinetics of fast chemical reactions, like photo-polymerization reactions.

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