A comparative study of polymerization lamps to determine the degree of cure of composites using infrared spectroscopy

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SUMMARY The aim of this study was to compare polymerization lamps of various technologies (halogen, high performance halogen, xenon, i.e. plasma arc, as well as diode lamps) to determine the degree of polymerization of composite probes using Fourier-transform infrared (FTIR) spectroscopy. To observe the light-induced curing reaction under a bracket, an attenuated total reflection (ATR)–FTIR was used.

The results showed that the recommended curing times for all the polymerization lamps tested were adequate for successful polymerization of the composite used (degree of conversion approximately 60 per cent, which did not exceed 66 per cent after longer curing times). However, even after very long curing times, delayed curing of the composite must be taken into consideration as there was a decrease of approximately 10 per cent in FTIR band intensities (1637 and 3104 cm⁻¹). ATR-FTIR spectroscopy showed that when bonding brackets with materials cured by light, uncured areas remain in the centre of the lowest layer of the adhesive.

Introduction

Halogen lamps have been routinely used to cure dental materials for over 20 years. By employing filters, visible light is obtained that has fewer side-effects, which is in contrast to ultraviolet light (Zigman *et al.*, 1973; Tavas and Watts, 1979).

Developments in polymerization lamps have recently taken place. Since 1995, laser light has also been offered to cure composite materials. In 1998, the plasma lamp, also known as the xenon arc lamp, came on to the market, and since 2000, light-emitting diode lamps (LEDs) have also been available.

In this study, a comparison of the various lamps was carried out by determining the conversion rate (i.e. the percentage of all double bonds converted during curing) dependent on the curing time as a measurement to assess the degree of polymerization. When curing dental composites that are based on acrylic or methacrylic resins, a free radical polymerization of the acrylate and methacrylate groups follows activation of a photo-initiator through light (Städler, 1994; Fouassier, 1995). During polymerization, the C=C double bonds are converted (Figure 1). The more double bonds that are converted, the higher the degree of polymerization and the curing of the composite. For a detailed review of photo-curable dental compositions, see Linden (1993).

The degree of curing, i.e. the conversion of C=C double bonds, can be assessed using infrared (IR) spectroscopy as a function of curing time. A convenient method has been developed using real-time IR spectroscopy to characterize the photo-curing behaviour of acrylic and methacrylic resins (Decker and Moussa, 1988).

General points concerning IR spectroscopy

IR, or heat radiation, is electromagnetic radiation which is invisible to the human eye and which borders on the visible spectral range to greater wavelengths. Its spectral range extends from 760 nm to 0.5 mm and triggers both vibrations and rotations in molecules.

Therefore, IR spectroscopy is based on the fact that molecules absorb electromagnetic radiation in the IR region. This molecular reaction is related to the presence of individual functional groups, which cause absorption bands in defined areas of the IR spectrum. In other words, a functional group can be identified by its IR absorption bands. The IR spectrum is a diagram describing the transmittance in percentage on the ordinate axis as a function of the wave number (the reciprocal wavelength; in cm⁻¹) on the abscissa. Alternatively, the absorbance $A = \log I_0/I$ can be indicated on the ordinate axis. Absorbance A follows (within certain restrictions) the Lambert–Beer Law ($A = \varepsilon bc$; where A is absorbance, ε is molar absorptivity with units of $1 \text{ mol}^{-1} \text{ cm}^{-1}$, b is the path length of the sample, c is the concentration of the compound in the solution, expressed in mol/l) and is directly proportional to concentration and coating thickness. The fundamentals of Fourier-transform IR (FTIR) spectroscopy are the recording of the total spectrum with an interferogram. The measurement principle is based on the Michelson interferometer. The beam of an IR light source (e.g. a silicon carbide 'globar') penetrates a sample and passes through a semipermeable interferometer plate. This functions as a beam splitter: it reflects one half of the incident radiation to a fixed mirror and the other half to a movable mirror. The



Figure 1 Free radical polymerization of methacrylates.

two reflected beams finally interfere and the interference signal depends on the position of the movable mirror. By recording the interference of all wavelengths present in the spectrum as a function of the position of the movable mirror, an interferogram is obtained. A mathematical process (Fourier transformation) converts the interferogram into a conventional IR spectrum (frequency domain) (Hesse *et al.*, 2002). In all cases, an IR spectrum is obtained as a plot of the IR intensity as a function of the frequency of the IR radiation. The frequency is usually expressed in wave numbers (cm⁻¹).

A special technique is attenuated total reflection (ATR)–FTIR spectroscopy. This is a reflection method which makes use of the physical phenomena of light reflection at the interface of two media of different indices of refraction.

The IR beam is coupled into a medium of high index of refraction (the ATR crystal) which is in intimate contact with a medium of lower index of refraction (the sample). The ATR crystal is usually made from silicon, germanium or thallium bromide/iodide (KRS5). The IR beam is reflected at the interface of the crystal and the sample. During reflection, the IR beam penetrates the surface layers of the sample. As the penetration depth amounts to a few micrometres (depending on the indices of refraction, the wavelength, and the angle of incidence), a surface IR spectrum of the sample is obtained. ATR-FTIR spectroscopy is useful for surface analysis and for samples which are difficult to prepare for transmission spectroscopy. For further information on IR sampling techniques, see Hesse et al. (2002), and for IR band assignments, Socrates (1994).

Materials and methods

Instruments

FTIR spectra were recorded with an FTIR spectrometer (PerkinElmer Spectrum One, PerkinElmer Inc., Norwalk, Connecticut, USA) (light source: silicon carbide; resolution 4 cm⁻¹). For ATR measurements, a single reflection ATR unit (Harrick Split Pea[™], Harrick Scientific Corp., New York, USA) was used. Harrick's

Split PeaTM is a horizontal internal reflection (ATR) accessory with the smallest sampling area of any ATR accessory, less than 250 μ m in diameter for its silicon ATR crystal. Both the emission spectra of the polymerization lamps and the ultraviolet–visible absorption spectra of the dental composites were recorded with a diode array spectrometer (Hewlett Packard HP 8452A, Hewlett Packard Corp., Palo Alto, California, USA), range 190–510 nm at a resolution of 1 nm.

For photo-curing, the following polymerization lamps were used:

- Halogen lamp: Optilux 401 (Kerr Corp., West Collins, Orange, USA), light intensity minimum 550 mW/cm², wavelength range 400–520 nm, recommended curing time: 2 × 20 seconds.
- 2. High performance halogen lamp: Optilux 501 (Kerr Corp.), light intensity 300–1100 mW/cm², wavelength range 400–510 nm, recommended curing time with booster mode 2×5 seconds at 1100 mW/cm² light intensity.
- Plasma (xenon) lamp: Apollo 95 E/Elite (DMD, Woodland Hills, USA), light intensity (curing mode) 1600 mW/cm², wavelength range (curing mode) 460– 490 nm, curing time: 2 × 1, 2 × 2 or 2 × 3 seconds.
- 4. Diode lamp (LED): GCeLight (GC Europe, Leuven, Belgium), light intensity 750 mW/cm², wavelength range 440–490 nm, selected curing time (fast cure mode) 2×9 , 2×12 seconds.

The emission spectra of the polymerization lamps are displayed in Figure 2.

Materials

The composite adhesive used was Enlight LV (+ Ortho Solo as the bonding agent) (Ormco Corp., West Collins, Orange, USA). This composite contains dimethacrylate monomer (20–30 per cent), alumosilicate glass filler (70–80 per cent) and additives (4 per cent), among them camphorquinone as the photo-initiator.

The brackets used were Optimesh XRT, 340-6807, slot 0.018, torque 0, angulation 0 (Ormco Corp.). The brackets had a meshed base and a base area of 13 mm².

FTIR measurements

Transmission measurements with the FTIR spectrometer were performed with samples of 40 μ m (to observe photo-induced polymerization by evaluation of two IR bands) and 200 μ m thickness (to compare the efficiency of the different lamps). The thickness of 200 μ m was chosen because it represents the highest tensile strength (Schiffer *et al.*, 1992). Using PTFE (polytetrafluoroethylene, available under the trade name Teflon) spacers, the sample was placed between two sodium



Figure 2 Emission spectra of (a) Optilux 401, (b) Optilux 501, (c) Apollo 95 E, (d) GCeLight.

chloride plates (thickness 4 mm; diameter 25 mm), which are translucent for both ultraviolet and IR radiation. Exposing the samples to light was carried out in such a way that the light conductor was brought into contact with one of the NaCl windows.

The IR source emits IR radiation, which is absorbed when penetrating the sample (Figure 3). The detector signal is electronically transformed into an IR spectrum, which then provides information about the composition of the sample.



Figure 3 The principal set-up of *in situ* infrared measurements of light-curable dental formulations (measurement in transmission).

ATR-FTIR spectroscopy for IR measurements of composite layers positioned under a bracket, and thus shielded from direct visible light, was employed (direct light exposure under a bracket is not possible). The principal set-up is shown in Figure 4. The sample was in contact with a single reflection ATR crystal made from



Figure 4 The schematic set-up of attenuated total reflection– Fourier-transform infrared (ATR–FTIR) measurements of a composite adhesive placed under a bracket.

silicon. The detector signal was converted into an ATR-FTIR spectrum which is similar, but not identical, to a transmission IR spectrum. The depth of analysis is in the range of a few micrometres.

In all experiments the spectra were converted to absorbance spectra. The absorbance A (i.e. the intensity) of selected IR bands was evaluated using the conventional tangent-fit method and by measuring the height of the signal.

Results

Emission spectra of the lamps

The composites currently used for light polymerization contain diketone compounds, mainly camphorquinone, as a photo-initiator, together with an amine as a reducing agent. The absorption spectrum of camphorquinone ranges from 350 to 550 nm in the visible range, and has an effective range of 400–500 nm and an absorption maximum at 468 nm (Städler, 1994). Ideally, the emission spectra of the lamp should match the absorption spectrum of camphorquinone, which is used as a polymerization initiator in dental photo-curable formulations. While halogen lamps cover the absorption area of the camphorquinone over a broader range, the xenon and LED lamps primarily emit light in a wavelength range that corresponds to the absorption maximum of camphorquinone (see Figure 2a–d).

Selection and correlation of IR bands

The initial experiments were carried out with 40 μ m adhesive coatings (Enlight) between two NaCl crystals. Light exposure was undertaken with the Optilux 401 with exposure times between 0 and 200 seconds. The 40 μ m coating, which is only a thin layer, allowed the IR signals to be followed both at 3104 and 1637 cm⁻¹.

Figure 5 shows that light-induced polymerization mainly occurs during the first few seconds of exposure.



Figure 5 Light-induced curing of the composite (40 μ m): normalized band intensities (absorbance data) at 1637 (\blacklozenge) and 3104 (\bigtriangleup) cm⁻¹ as a function of exposure time.

The intensity of the IR band at 3104 cm⁻¹ decreased to a lower level than the intensity of the band at 1637 cm⁻¹. After prolonged light exposure (200 seconds) the band at 1637 cm⁻¹ decreased to 52 per cent of its original intensity, whereas the band at 3104 cm⁻¹ decreased to approximately 37 per cent of its original amplitude. One reason for these differences may be a superimposition of various IR bands in the spectral ranges under consideration—especially in the 1600–1650 cm⁻¹ range, various C=O, C=C and other bands overlap. In this case, data on the conversion of methacrylates may be incorrect when a simple tangent-fit is applied to set the baseline. A good correlation was, however, obtained between the absorbance data at 1637 and 3104 cm⁻¹. Figure 6a contains details of FTIR spectra of the composite after different light exposure times which show the shape of the band at 1637 cm⁻¹ after various illumination times. A similar plot for the band at 3104 cm⁻¹ is presented in Figure 6b. It is evident from both



Figure 6 (a) Infrared spectrum of the composite (40 μ m film thickness) in the range 1560–1660 cm⁻¹. The decrease in C=C signal at 1637 cm⁻¹ results from the light-induced polymerization reaction. (b) Infrared spectrum of the composite (200 μ m film thickness) in the range 3000–3145 cm⁻¹. The decrease in the bands at 3104 and 3030 cm⁻¹ (=CH₂ stretching vibrations) results from the light-induced polymerization reaction. 0, uncured composite; 40, 40 seconds of irradiation; 200, 200 seconds of irradiation; 200+, 200 seconds of irradiation followed by 24 hours' storage at room temperature.



Figure 7 Ultraviolet–visible transmission of a 200 μ m composite film. A, before photo-curing; B, the same film after 200 seconds of irradiation.

plots that polymerization reactions also occur after illumination (post-curing reaction). When an illuminated (200 seconds) sample was stored for 24 hours at room temperature, the band intensities decreased to 42 (1637 cm^{-1}) and 29 (3104 cm^{-1}) per cent of their initial values.

Photo-curing of a dental composite using different lamps

In order to compare the curing efficiency of various commercial lamps, the progress of photo-polymerization was recorded using FTIR spectroscopy. For this investigation, composite films of 200 µm thickness were employed, as this thickness is common in practical applications. The ultraviolet-visible spectrum of the composite material (200 µm film thickness) indicated low transmission (less than 1 per cent) (Figure 7). This low transmission can be explained by the high content of silicate filler, which leads to strong scattering of the light. As a result of curing by visible light, the transmission decreased even further (Figure 7). As the light intensity is low in deeper layers of the composite films, special care has to be taken when thick films are to be light cured. With 200 µm films it proved advantageous to monitor the IR band at 3104 cm⁻¹ (=CH₂ asymmetric stretching vibration of methacrylates) during illumination. The measurements were performed in transmission, as shown in Figure 3.

The results are displayed in Figure 8. Using the recommended or chosen curing times, all the tested lamps achieved a residual acrylate content of approximately 40 per cent (Optilux 401 even 35 per cent) which did not drop below 34 per cent at longer curing times (200 seconds).

The decrease in band intensities showed curing effects after light exposure. Even after long illumination times



Figure 8 Photo-curing of the dental composite (200 µm film) using various lamps. Normalized intensity of the infrared band at 3104 cm⁻¹ as a function of the irradiation time; the solid symbols indicate the photo-curing time recommended by the manufacturers of the lamps (\diamond , Apollo 95E; \triangle , GceLight; \Box , Optilux 401; \circ , Optilux 501).

(200 seconds with Optilux 401) the intensity of the band at 3104 cm⁻¹ continued to decrease during 24 hours of storage at room temperature (cf. Figure 6b). The final band intensity was approximately 29 per cent of its initial value, which proved that post-curing reactions contribute to the overall curing reaction in the composite material under investigation.

Photo-curing of a dental composite placed under a bracket

It is common to fix dental brackets with photo-curable composite adhesives so that the adhesive is shielded from direct light. In the zones centred under the bracket, only scattered and reflected light can penetrate into the composite. The strongly reduced light intensity in these zones makes it doubtful whether the photocuring process can proceed correctly and whether the desired adhesion is obtained. To investigate the photopolymerization in shaded areas, the ATR-FTIR set-up shown in Figure 4 was used. As the depth of analysis amounted to 1-7 µm in the ATR experiment, it was possible to assess the IR band at 1637 cm⁻¹ in order to follow the progress of photo-initiated polymerization. The light guides of the polymerization lamps were adjusted in such a way that the irradiation of the samples occurred at an angle of approximately 45 degrees. The brackets covered an area of 13 mm²

A reference measurement using a glass slide (transmissive for wavelengths greater than 300 nm) instead of the bracket showed that approximately 50 per cent of all methacrylate groups were converted after 20 seconds of illumination. In the experiments with the composite shielded by the bracket it was not possible to achieve any conversion with the GCeLight, Optilux 401, and Optilux 501 lamps, even after very long curing times (more than 100 seconds) (Figure 9). On the other hand,



Figure 9 Photo-curing of a dental composite placed under a bracket: normalized intensity of the band at 1637 cm^{-1} as a function of the irradiation time using different lamps [\diamond , Apollo 95E; \triangle , GCeLight; \Box , Optilux 401; \circ , Optilux 501: *, Optilux 401 reference (glass)].

the Apollo 95E lamp achieved a reduction in the IR signal by 10 per cent at 1637 cm⁻¹ after a 40 second curing period. After 76 seconds of exposure, a residual acrylate content of 61 per cent was determined. This may have been due to an unnoticed change in the position of the bracket, which led to altered illumination conditions near the position of the ATR crystal.

Discussion

The usual procedure for photo-induced curing of composites which contain acrylate or methacrylate is to analyse the C=C valence vibration band at 1620-1640 cm⁻¹ or a band in the spectral range between 800 and 1000 cm⁻¹ which originates from =C-H bending vibrations. However, inorganic fillers cause additional strong absorption in the IR range 1000-800 cm⁻¹. Consequently, the IR band typical of =C-H bending vibrations of acrylic and methacrylic units cannot be assessed as it is obscured by the strong IR absorption of the inorganic filler. With the thick films of composite material (200 µm) used in this study, it was also difficult to quantify the C=C valence vibration band at 1620-1640 cm⁻¹ due to total absorption in this spectral range. However, with films of 40 µm thickness, this band could be analysed without problems. In a similar way, it was possible to monitor this IR band in ATR experiments, as the penetration depth of the IR beam amounted to a few micrometres.

As an alternative, two weak IR bands at 3104 and 3030 cm⁻¹ can be assessed. These bands are assigned to the asymmetrical and symmetrical stretching bands of =CH₂ units in methacrylates. Both these IR bands disappear during polymerization and can also be monitored in thick composite layers (200 μ m). In the set-up under investigation, the signal at 3104 cm⁻¹ was not overlapped by other bands, which made quantitative assessment possible. In thin layers, however, or in the ATR experiment, the band intensity was too weak to be analysed.

Conclusions concerning the transformation of the methacrylate functions in the dental composites under investigation must be made with caution when based on IR data. However, comparisons of experiments performed with various lamps were possible. Post-illumination curing effects in these composites have been demonstrated by IR spectroscopy.

Tarle et al. (2002) also pointed out a significantly higher degree of conversion with conventional curing with a halogen lamp (degree of conversion 60.0 ± 2.5 and 73.5 ± 1.4 per cent after 20 and 40 seconds of illumination, respectively) compared with LED (degree of conversion 54.9 ± 1.3 to 65.4 ± 2.4 per cent after 20 and 40 seconds of illumination) and the rapid plasma arc light (degree of conversion 53.8 ± 2.7 to 69.7 ± 5.5 per cent after 1, 2, and 3 seconds of curing time). Although there were significant differences in the light intensities between their LED lamp (9 mW/cm²), the plasma arc light (1370 mW/cm^2) and the halogen lamp (560 mW/cm^2) , similar degrees of conversion were achieved using the LED and the plasma arc lamp. This was explained by the better match of the spectral absorption of camphorquinone and the emission of the LED lamp (Tarle et al., 2002).

However, camphorquinone absorbs between 350 and 550 nm, peaking at 468 nm (Städtler, 1994). The results of the present study show that both LED and plasma arc lamps emit light in a wavelength range that corresponds to the absorption maximum of camphorquinone, while halogen lamps broadly cover the absorption area. In contrast to Tarle *et al.* (2002), a LED lamp with a light intensity of 750 mW/cm² and shorter curing times $(2 \times 9 \text{ and } 2 \times 12 \text{ seconds})$ were used in the present investigation. Regarding the reciprocal relationship between power density and exposure time over a certain timeframe (Halvorson *et al.*, 2002), similar degrees of acrylate conversion are achieved when the energy density is identical (at constant spectral distribution of the light source).

When the dental composite was placed under a bracket, ATR-FTIR spectroscopy showed that limited photo-induced polymerization occurred. It must be stated that using the ATR crystal (approximately 0.3 mm in diameter) only the photo-induced reactions at the very centre of the area covered by the bracket (base area 13 mm²) were monitored. It is clear that some light will penetrate into the dental composite near the rim of the bracket which provides photo-curing sufficient to ensure adhesion of the bracket to the enamel. Moreover, it has to be taken into account, that, compared with this ATR experiment, light reflection may be different when the dental composite is placed between a bracket and dental enamel. However, the present experiments indicate that dark areas may remain under brackets where curing of the composite is insufficient.

Conclusions

It can be concluded that with the recommended or chosen curing times, maximum methacrylate conversion with this dental composite can be achieved.

Thus, the lamps investigated are adequate for polymerization of the investigated methacrylate-based dental composite. With both 40 and 200 μ m composite films, the polymerization reaction is almost complete when applying the recommended irradiation times.

However, delayed curing of the composite must be taken into account, even after very long photo-curing times. When bonding brackets with photo-curable materials, insufficiently cured areas may remain at the centre of the area covered by the bracket. This was indicated by *in situ* ATR IR measurements during illumination.

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