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Degree of cure of orthodontic adhesives with various polymerization initiation modes

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SUMMARY The purpose of this study was to estimate the degree of cure (DC) of a light-cured, and a two- and a one-phase (no-mix) chemically-cured, as well as a dual-cured commercially available orthodontic adhesive resin. Forty stainless steel brackets were divided into four groups of 10 brackets each, and the bracket bases were covered with a standardized volume of adhesive. They were then pressed firmly onto a yellowish background surface of 75 per cent reflectance covered with cellulose film to facilitate detachment of the system and recovery of the set material. The visible light- and dual-cured adhesives were photopolymerized by irradiation from the incisal and cervical edges of the bracket for 10 seconds each, while another group of ceramic brackets was used to assess the differential interference of transparent relative to opaque material in the DC. Micro-multiple internal reflectance Fourier transform infrared spectroscopy was employed for the estimation of the DC of the adhesives ($\alpha = 0.05$, $n = 10$), utilizing a method proposed previously. The dual-cured product demonstrated the highest DC followed by the light-cured combined with the ceramic bracket, and the no-mix and the chemically-cured adhesives. The combination of the metallic bracket with the light-cured product resulted in a DC comparable with that of the chemically-cured material.

Introduction

Despite the numerous studies investigating the bond strength provided by various combinations of orthodontic adhesive resins and ceramic or stainless steel brackets, limited information has been presented with regard to the degree of cure (DC) of the polymeric material (Eliades *et al.*, 1995). This parameter is considered a key factor in modulating the profile of the material, including a wide array of mechanical properties (Ferracane and Greener, 1986) and potential biological adverse reactions (Rathbun *et al.*, 1991). The latter has recently gained special interest in the light of new evidence that some resins may release bis-phenol A, a bis-GMA monomer precursor, which exhibits estrogenicity (Olea *et al.*, 1996). The assessment of the DC of polymeric adhesives is of importance because of the association of a low DC with the development of a weak polymer network, possibly allowing release of substances with toxic effects.

The hypothesis tested in this study was that the various polymerization initiation modes of orthodontic adhesives impact on their DC. The purpose of this investigation was to estimate the DC in a light-cured, and a two- and a one-phase (no-mix) chemically-cured, as well as a dual-cured commercially available adhesive resin.

Materials and methods

Four types of orthodontic adhesives were selected for the study; their commercial names and modes of polymerization are shown in Table 1. Forty stainless steel upper incisor brackets (Diamond, Ormco, Glendora, CA, USA) were divided into four groups of 10 brackets each. The bracket bases were covered with a standardized volume of adhesive and then pressed firmly on a

Table 1 The orthodontic adhesives included in the study.

Product	Manufacturer	Polymerization mode
Concise	3M/Unitek	Two-paste, chemically-cured
DuoCement	Coltene	Two-paste, dual-cured
Transbond XL*	3M/Unitek	One-paste, light-cured
Unite	3M/Unitek	One-paste (no-mix), chemically-cured

*Transbond XL adhesive was used for both stainless steel and ceramic bracket bonding.

yellowish background surface with a 75 per cent reflectance, and covered with cellulose film to facilitate detachment of the system and recovery of the set material. The excess resin was carefully removed before polymerization.

The visible light- and dual-cured adhesives were photopolymerized utilizing a light curing unit (Elipar Visio II, Espe GmbH, Seefeld, Germany) emitting 650 mW/cm^2 light intensity at 468 nm as measured with a curing radiometer (Model 100, Demetron Corp., Danbury, CT, USA). Irradiation was performed from the incisal and cervical bracket edges for 10 seconds each side. A further 10 ceramic brackets (Allure IV NSB, GAC Int., Central Islip, NY, USA) bonded with the light-cured adhesive with the same irradiation mode, were prepared to assess the differential interference of transparent relative to opaque brackets in the degree of cure. All bonding procedures were performed by an orthodontist.

The bonded brackets were stored for 5 minutes at 37°C and 50 per cent relative humidity. After setting, the cellulose strips were removed and the resultant adhesive flat surfaces, corresponding to the material in contact with the substrate (enamel in clinical conditions), were analysed by micro multiple internal reflectance Fourier transform infrared spectroscopy (micro-MIR FTIR). The flat surfaces were pressed against the sampling surface of a KRS 5 mini-crystal of a micro-MIR FTIR accessory (Perkin-Elmer Corp., Norwalk, Conn., USA). The accessory was then placed on a FTIR spectrometer (P-E 1760X FTIR) interfaced to a data station. From each resin surface, spectra were recorded under the following conditions: 4000–400 cm^{-1} wavenumber range, 4 cm^{-1} resolution, 30 scan transients. The mean sampling depth of the micro-MIR technique was estimated as 3 μm at 1000 cm^{-1}.

Spectra were also acquired from 10 specimens of unpolymerized pastes of the adhesives which served as a reference. For the two component systems equal amounts of base and catalyst pastes were placed in contact with a nominally equal area of each of the two sides of the KRS-5 mini-crystal. The resultant spectra simulated the mixed monomer content without interference from the polymerization process.

The DC of each specimen was estimated on a relative percentage basis with the two frequency method and the tangent baseline technique (Rueggeberg *et al.*, 1990). Aliphatic (C=C) bond stretching vibrations at 1638 cm^{-1} were chosen as the analytical frequency, whereas the aromatic (C..C) bond stretching vibrations at 1605 cm^{-1}, which are not affected by the polymerization reaction, were selected as a reference frequency. The percentage DC was then determined according to the equation:

$$\%\mathrm{DC} = 100 \cdot 1 - \frac{Ap(\mathrm{C{=}C}) \times Am(\mathrm{C..C})}{Am(\mathrm{C{=}C}) \times Ap(\mathrm{C..C})}$$

where Ap(C=C) is the net peak absorbance area of the set material at 1638 cm^{-1}, Am(C..C) is the net peak absorbance of area of the unset material at 1605 cm^{-1}, Am(C=C) is the net peak absorbance area of the unset material at 1638 cm^{-1}, and Ap(C..C) is the net peak absorbance area of the set material at 1605 cm^{-1}.

The statistical analysis of the results was performed by one-way ANOVA and Tukey multiple comparisons test at $\alpha = 0.05$ significance level.

Table 2 The percentage degree of cure (%DC) of the adhesives included in the study ($\alpha = 0.05$, $n = 10$).

Product	%DC ± 1 SD	Tukey grouping*
DuoCement	68 ± 3.4	A
Transbond XL (ceramic bracket)	58 ± 3.2	B
Unite	58 ± 4.6	B
Concise	52 ± 5.6	C
Transbond XL (metallic bracket)	48 ± 4.3	C

*Means with same letters are not significantly different at $\alpha = 0.05$ level.

Results

Table 2 shows the DC values obtained for the materials used in the study. The dual-cured product demonstrated the highest DC followed by the light-cured combined with the ceramic bracket, then the no-mix and the chemically-cured adhesive. While the combination of metallic bracket with the light-cured adhesive showed the least DC, the value obtained was comparable to that of the widely used Concise adhesive.

Discussion

The micro-MIR FTIR technique employed in this study to investigate the degree of carbon-carbon double bond conversion is an essential surface analytical method (Roberts, 1992). In a clinical situation, the surface of the adhesive subjected to analysis in this study would be in contact with the enamel.

For a given monomer system, the thickness of the adhesive layer and the temperature should have an effect on DC, with the higher temperatures and thinner layers having higher conversion rates. Adhesive resins containing low molecular weight monomers and relatively low filler volume content should form thinner layers as a result of lower viscosities. This difference is anticipated from the much higher viscosities of the heavily filled composites, which require increased compressive forces to cause thinning of the material. In the present study, the ambient temperature was constant throughout the spectroscopic analyses. In addition, a relatively consistent thickness of the adhesive layer was achieved with the application of firm finger pressure on the same bracket base (Eliades *et al.*, 1991).

The use of natural teeth instead of the artificial background surface employed in this investigation would have caused additional complexity from variables such as surface topography and roughness, the related difficulty in detaching the resin for analysis, and the variability in optical properties for the tooth enamel. With the present non-destructive approach, the background surface did not introduce an additional experimental variable, and its influence was nominally identical during each experiment (Eliades *et al.*, 1995).

Despite the statistically significant difference noted, the DC for the light-cured adhesive layer bonded to the opaque stainless steel bracket was within the range of the DC for the adhesive layers bonded to the translucent polycrystalline alumina brackets. These observations may be explained by considering several aspects of polymerization variables for this material: the adhesive was exposed to light primarily from the light-curing unit and, secondly, from back-scattering from the artificial background surface (Fan *et al.*, 1994). Indirect curing of the adhesive from the incisal and cervical edges of the bracket, as employed in this study, might have decreased the optical path compared with photo-activation from the mesial and distal edges, since rectangular-shaped brackets were used.

A previous report based upon micro-hardness tests claimed that secondary illumination is of very low intensity and insufficient to induce adequate conversion (Cheng *et al.*, 1989). However, the mode of light application in that study was exclusively from the lingual surface of the tooth and, therefore, not comparable with this investigation. Although the interference of the bracket dramatically reduces the intensity of the available light, the adhesive to be cured has a very low thickness.

Previous research has proposed the concept of a critical light transmittance and a 'threshold' light intensity with curing adhesives for ceramic brackets (Eliades *et al.*, 1995). The latter has to be attained in order for the polymerization to be initiated. This result is presumably due to the thin film nature of the adhesive layer, which has a very high surface-to-volume ratio. The dominance of surface properties over bulk adhesive properties is considered to favour the use of light-cured resins, because these systems are expected to possess superior surface characteristics (Ruyter, 1985).

The principle of inhomogeneous polymerization was introduced in orthodontics with the development of the no-mix bonding resins, which were intended to minimize the mixing-induced defects and to reduce the steps required for application of the material. These defects owe their presence to the excessively prolonged exposure to atmospheric conditions and the trapping of air bubbles during mixing. Mixing has long been known as a factor that results in compromised properties. Studies have shown that photo-cured composites, intentionally mixed as if they were chemically-cured materials, demonstrated porous surfaces and air voids in the bulk material (Merkel, 1983).

In the no-mix systems, a catalyst gradient is formed from the primed enamel surface towards the brackets, through a diffusion process. Under these conditions, the resin strength is supposedly decreased due to the establishment of a disturbed cross-linked network, which nonetheless may facilitate bonding. This may be attributed to the increased surface-to-volume ratio of orthodontic adhesives which accompanies their application. One of the few studies investigating this parameter, showed that adhesive layer thickness prepared under simulated clinical conditions may not exceed 250 μm depending on the morphology and design of the bracket base (Eliades *et al.*, 1991). Thus, the behaviour of the adhesive layer may be approximated by a two-dimensional material surface where bulk material properties are not expressed. This assumption is a cornerstone hypothesis for the use of the no-mix systems. Due to the previously analysed structure it is presumed that by applying the bonding agent to the tooth surface and bracket base, the material may be polymerized by a diffusion process intensified by pressing the bracket to the enamel. However, it may be worth noting that the technique employed in this study analyses the surface of optimum conversion for the no-mix adhesive.

In the modern orthodontic practice, the time required for the clinical application of these materials is an essential parameter. This varies considerably among the types tested, with the dual-, light-, and chemically-cured adhesives being the most time-consuming. Since there is a notable lack of standards associated with the required DC derived from clinical conditions, the use of materials possessing higher DC rates may not justify the incorporation of lengthy procedures, especially when the differences noted are relatively small. The results of this investigation viewed from a different perspective could support the use of one-phase, no-mix adhesives based on the DC values obtained from this material which are comparable with the DC demonstrated by the dual-cured adhesives. Further research focusing on the *in vivo* failure rate of brackets bonded with no-mix adhesives is required to clarify the efficiency of this adhesive system.

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