

THE INFLUENCE OF FREE-RADICAL CONCENTRATION ON THE SHEAR BOND STRENGTH OF DENTAL COMPOSITES

VPLIV KONCENTRACIJE PROSTIH RADIKALOV NA STRIŽNO TRDNOST DENTALNIH KOMPOZITOV

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The aim of this study was to evaluate the influence of the free-radical concentration on the shear bond strength between a composite resin and self-adhesive composite cement. Filtek ultimate flowable restorative composite was used for the thin layer samples, which were analyzed using electron paramagnetic resonance (EPR). Rely-X-Unicem cement was applied to the disc-shaped samples and the shear bond strength and failure modes were analysed at weekly intervals. The concentration of the free radicals dropped to 10 % after 24 h. A value for the degree of conversion equal to 74 ± 2 % was achieved after 2 d. The shear bond values were in the range from 25.5 ± 3.7 MPa to 9.8 ± 4.3 MPa for four groups of samples, measured in four different time intervals. A high concentration of free radicals ensures reliable chemical bonding with a freshly applied cement in group 1, while in the samples of group 2 (7 d), group 3 (14 d) and group 4 (21 d of recombination in water), the potential of the free radicals was diminished.

Keywords: composite resin, free radicals, electron paramagnetic resonance, degree of conversion, shear bond strength, adhesion properties

Namen raziskave je bil proučiti vpliv koncentracije prostih radikalov na moč vezave med kompozitom in samostrjujočim se kompozitnim cementom. Kompozit Filtek ultimate flowable restorative smo uporabili za pripravo vzorcev v tanki plasti za meritve koncentracije prostih radikalov z elektronsko paramagnetno resonanco (angl. EPR). Na kompozitne diske smo nanесли kompozitni cement Rely-X-Unicem in v tedenskih intervalih merili moč vezave med obema materialoma. Koncentracija prostih radikalov se je v 24 urah zmanjšala na 10 % začetne koncentracije. Stopnja konverzije (DC) se je po dveh dneh ustalila pri 74 ± 2 %. Moč vezave med obema kompozitoma je bila v območju med 25.5 ± 3.7 MPa in 9.8 ± 4.3 MPa za štiri skupine vzorcev. Visoka koncentracija prostih radikalov zagotavlja dobro kemično vezavo s sveže dodanim kompozitnim cementom, medtem ko je vpliv koncentracije prostih radikalov po (7, 14 in 21) dneh rekombinacije zanemarljiv.

Ključne besede: kompozit, prosti radikali, elektronska paramagnetna resonanca, stopnja konverzije, strižna trdnost, adhezijske lastnosti

1 INTRODUCTION

In a daily practice, clinicians frequently need to apply a fresh layer of methacrylate-based composite over an already-existing and aged composite. This commonly happens in two main clinical situations: (a) when a selective repair, instead of the a complete replacement of a failed direct composite restoration is carried out, or alternatively, (b) when indirect restorations are adhesively cemented onto protected dentin according to the principles of the a dual dentin bonding or, as also named, the immediate dentin-sealing (IDS) technique.^{1,2}

The chemical bonding of the composite resin matrices is formed by the unreacted methacrylate groups and/or the free radicals present in the underneath composite layer.^{3,4} The extent of the monomer-to-polymer conversion during the polymerisation process is expressed as the degree of conversion (DC) and can be studied by Raman spectroscopy, which measures the C=C double bond's stretching vibrations on the compo-

site surface.^{5,6} Consequently, the DC is directly related to the mechanical properties of the composites and their clinical performance.^{7,8}

Free radicals are reactive chemical species with an unpaired electron. Their interactions promote the development and cross-linking of the polymer chains that create a solid unit.⁹ However, as the composite substrate ages, the free radicals decay over time.³ As a consequence, the tendency for chemical bonding with a freshly applied composite layer decreases.⁴ Although it has never been directly proven experimentally, several authors have speculated that the concentration of the active free radicals remaining in the underlying layer is an important factor when it comes to achieving sufficient bonding in the composite.^{3,4,10} However, there are other mechanisms described in the literature regarding the bonding between the layers of the same composite or different kinds of composite materials, such as a micro-mechanical bond or an interpenetrating polymer network matrix.^{10,11}

The most suitable method for studying free radicals in various materials is electron paramagnetic resonance (EPR) spectroscopy. The unpaired electrons localised at the free radicals serve as precise local probes at the molecular level, providing information about the nature of the free radicals, their intensity and evolution over time.¹² The free radicals in methacrylate resin-based composites are well documented in the literature.⁹ The unpaired methacrylic electron is localized on the carbon atom and significantly overlaps with the protons of the nearest CH₂ and CH₃ groups, thus resulting in a characteristic EPR spectrum. The free-radical concentration is directly proportional to the intensity of the EPR signal.¹² This method was successfully employed in a study of the curing time of visible-light-activated composites as a function of the sample thickness as well as in other investigations involving dental composites.^{13–16}

The influence of the free-radical concentration in the underneath composite layer on the effectiveness of the bonding between dental composites has not been investigated yet. Therefore, the aim of our study was to clarify the role of the free-radical concentration on the shear bond strength between two layers of composite using the EPR method and simultaneously to verify the polymerisation process by measuring the DC using Raman spectroscopy.

2 METHODOLOGY OF THE EXPERIMENTAL WORK

In order to simulate the cementation process when the IDS technique is used in clinical practice, Filtek Ultimate Flowable Restorative (3M ESPE, St. Paul, MN, USA) was used as the underneath layer and the self-adhesive, dual-cure, Rely X Unicem (3M ESPE, Seefeld, Germany) cement as the freshly applied composite on top of it. The flow composite material was used in accordance with the recommendations, with the IDS technique as the material most appropriate to block out the undercuts of the prepared tooth. The self-adhesive cement Rely X is gaining in popularity among clinicians due to its effectiveness and simplicity of use.

2.1 Electron paramagnetic resonance (EPR) spectroscopy

The EPR spectra of the Filtek Ultimate Flowable Restorative composite samples were measured after light activation with a blue-phase G2 LED curing light with an output intensity of 650 mW/cm² (Ivoclar Vivadent, Schaan, Liechtenstein) (Figure 1). A relative comparison of the free-radical concentrations in composite samples was obtained by comparing the signal intensities to the same reference EPR sample. We used the so-called "strong pitch" (Bruker GmbH, EPR Division, Rheinstetten, Germany), which is commonly used as a standard sample in EPR spectroscopy for measuring the EPR signal's intensity.

In our study we used a Varian E-9 (Varian, Palo Alto, CA 94303, USA) EPR spectrometer that was partially

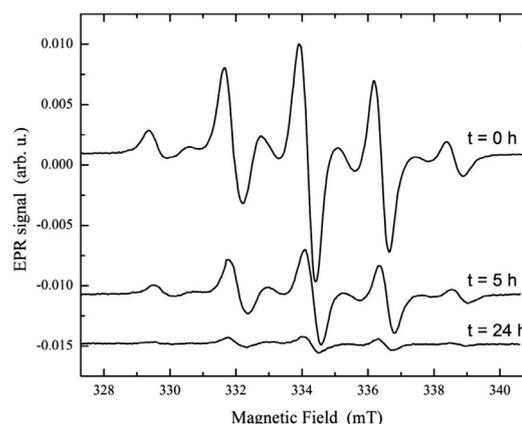


Figure 1: X-band electron paramagnetic resonance (EPR) spectra of methacrylate-based composite measured at ambient temperature immediately after light polymerisation ($t = 0$), 5 h ($t = 5$) and 24 h ($t = 24$) after polymerisation

upgraded. The EPR measurements were performed at an ambient temperature of 20–23 °C. In order to obtain the absolute value of the free radicals, we calibrated the intensity of the composite EPR signal by a comparison with a CuSO₄·5H₂O standard. We estimated the error of the absolute EPR signal intensity to be around 10 %.¹²

The application of the Filtek Ultimate Flowable Restorative composite using a micro-brush on a quartz plate (3 mm × 10 mm) produced an approximately 0.15-mm-thick layer (measured with a digital calliper), which is similar to previous studies that reported thicknesses of 60–80 μm to 200–300 μm, respectively, on convex and concave cavity surfaces for an IDS.¹⁷

The total illumination time was 120 s. Each sample was light activated in 5-second intervals in a cumulative manner. After each illumination the EPR spectrum was recorded and the radical intensity was calculated.¹² The samples were kept in water at a constant temperature of 37 °C to promote the recombination of free radicals and were temporarily removed from the water bath for each measurement in order to record the EPR spectrum.

2.2 Degree of conversion (DC)

Measurements of the Raman spectra were performed on a dispersive Raman spectrometer LabramHR (Horiba Yobin Yvon S.A.S. Molecular & Microanalysis Division, Villeneuve d'Ascq, France). We selected the spectral region from 1500 cm⁻¹ to 1700 cm⁻¹, where the C=C stretching vibrations are expected. Three composite discs, 6 mm in diameter and 2 mm thick, from the Filtek Ultimate Flowable Restorative, and a drop of the same non-polymerized composite resin on a glass plate were the samples for the Raman spectra measurements. For every composite disc the Raman scattering was measured at three different spots.

The specimens were excited with red laser light at $\lambda = 633$ nm and a low power of between 1 mW and 10 mW. The spectrum resolution was 1 cm⁻¹. The Raman vibrational modes were found (Figure 2): the stretching mode at 1640 cm⁻¹ is ascribed to the aliphatic

carbon-carbon double bond (C=C), as the analytical frequency, while the peak at 1610 cm^{-1} corresponds to the stretching of the aromatic C=C bond, and was used as the reference frequency. The intensities of these two modes were used to determine the DC as follows: the Raman peaks at 1640 cm^{-1} and 1610 cm^{-1} were fitted with the Gaussian line shapes to obtain their intensities by integration. The percentage of uncured resin R was calculated from the ratio of the intensities for the 1640 cm^{-1} and 1610 cm^{-1} peaks for the cured and the uncured samples, and finally the DC was calculated as Equation (1):

$$\text{DC} = 100 \times [1 - (R_{\text{polymerised}} / R_{\text{unpolymerised}})] \quad (1)$$

2.3 Shear-bond-strength (SBS) testing

The composite samples (Filtek Ultimate Flowable Restorative) were prepared directly into the disc-shaped cavities 6 mm in diameter and 2 mm thick in acrylic carrier cylinders. The surface was covered with a Mylar strip to minimise the formation of an oxygen-inhibited layer and to form a flat surface, by which the micro-mechanical interlocking at the bonding interface was reduced to a minimum. To polymerise the composite 40 seconds of light activation was applied. Immediately after the curing of the 10 composite discs (group 1), quartz cylinders with an inner diameter of 3 mm and a height of 4 mm were placed on the flat upper surfaces of the discs and carefully filled with the dual-cure, self-adhesive, resin cement Rely X Unicem. The cement was then left to polymerize chemically for 1 hour. Light polymerization was intentionally avoided because we wanted to prevent the eventual creation of additional free radicals within the underneath composite layer. The bonded samples were placed in a water bath at $37\text{ }^{\circ}\text{C}$ for 24 h. After the quartz cylinders were carefully taken off and the samples were stressed in an Instron testing machine (Instron 4301, Instron Corp., USA) until failure

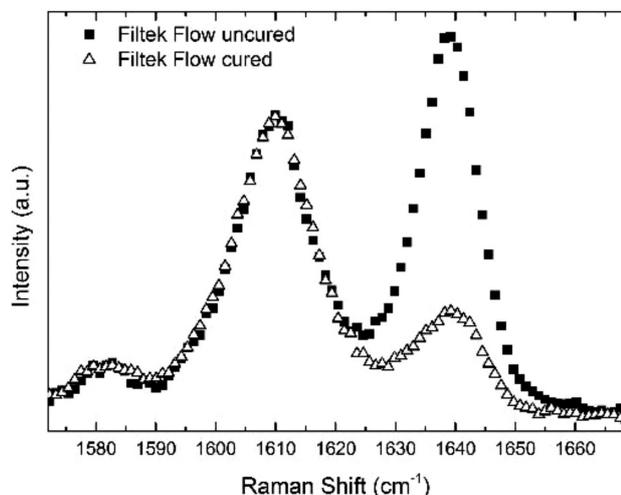


Figure 2: Overlay graph of Raman spectra of cured (triangles) and uncured (squares) Filtek ultimate flowable restorative composite samples

at a cross-head speed of 1 mm/min. The obtained bond strength is expressed in mega Pascals (MPa).

The rest of the three groups of 10 composite sample discs were stored in water at $37\text{ }^{\circ}\text{C}$ for up to 21 d. Shear bond measurements were performed every 7 d on 10 different disc samples and the same procedure for the shear-bond evaluation was implemented as previously described for the first group of samples. All together 40 composite discs (4 groups of 10) were used in the study in four different time intervals

2.4 Microscopic evaluation

The mode of failure was evaluated using an optical microscope (Stereo Discovery V.8, Carl Zeiss, Germany) at $20\times$ magnification. The failures were recorded as cohesive (fracture predominantly inside the composite disc) or adhesive (fracture predominantly at the interface between the composite cement and the composite disc).

2.5 Statistical analysis

Descriptive statistics, the ANOVA test, and the Bonferoni Post-Hoc test were used to interpret the SBS results in the present study. To compare the cohesive and adhesive failure mode in each time interval an independent t-test was used. For the correlation between the radical concentration and the shear bond strength the Spearman correlation test was used. A p value of <0.05 was considered as statistically significant.

3 RESULTS

3.1 Electron paramagnetic resonance (EPR) spectroscopy

The formation of the free radicals as a function of the light activation time in the Filtek Ultimate Flowable Restorative samples with thicknesses of 0.15 mm is represented by the triangles in **Figure 3**. The full saturation with free radicals was achieved after 40 s. The concentration was normalized to the saturated value, which was reached after an illumination time of 120 s. The absolute value of the saturated intensity of the EPR signal corresponds to a concentration of 5×10^{18} free radicals per 1 g of composite material.

The recombination dynamics of the free-radical concentration in the thin layer composite is presented as triangles in **Figure 4**. The normalized radical concentration dropped to 50 % after 5 h and it further dropped to less than 10 % after 3 d.

3.2 Degree of conversion

The DC of the composite increased sharply during the first 40 s of the illumination to reach a value of 47 %. Longer illumination times resulted in a smaller additional increase in the DC, and after 120 s of illumination the DC only increased to 50 % (**Figure 3**). During the so-called post-polymerization stage, 2 d after the

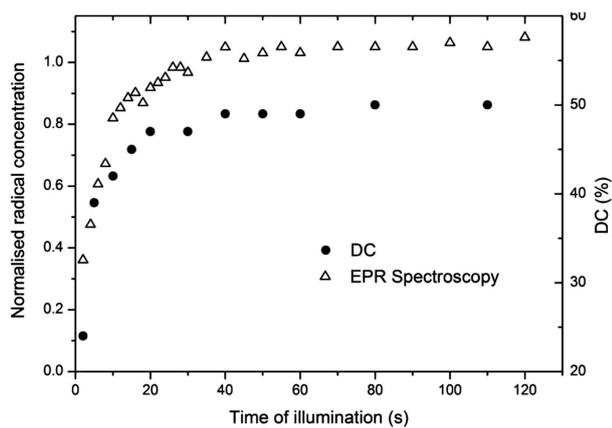


Figure 3: Normalized free-radical concentration measured by electron paramagnetic resonance (EPR) versus time of light activation in Filtek ultimate flowable restorative composite with a thickness of 0.15 mm (triangles); for comparison, the time dependence of the increase in degree of conversion (DC) after light activation is presented on the same time scale (circles)

illumination of the samples, the DC reached a value of $74 \pm 2\%$, while changes in the DC were not detected after a longer post-polymerization stage time (Figure 4).

3.3 Shear bond strength (SBS)

The SBS measurements for the four sample groups are presented in Figure 5. The mean value for the shear bond strength for the first group of samples with a saturated concentration of free radicals was 25.5 (SD 3.7) MPa. The samples of the second group showed a mean shear bond value of 20.3 (SD 6.7) MPa after a 7-day recombination in water at a temperature of 37 °C. After 14 d of exposure to water the shear bond values of the group 3 samples fell to 16.4 (SD 6.8) MPa. The fourth group of samples exposed to water for 21 d had shear bond values of 9.8 (SD 4.3) MPa.

The ANOVA test was used to reveal the statistically significant differences between the shear bond strengths

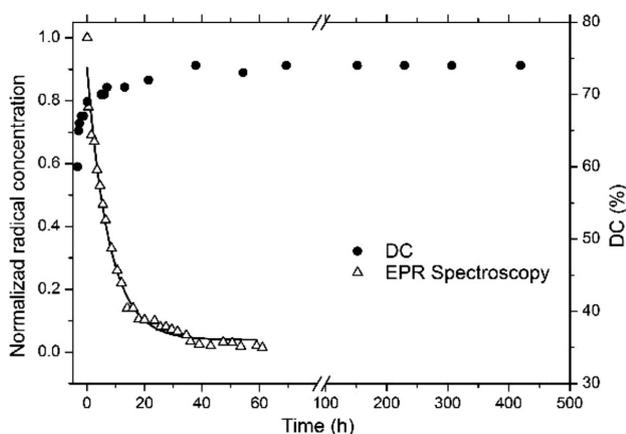


Figure 4: Recombination of normalized free-radical concentration in the Filtek ultimate flowable restorative composite in water (triangles); the degree of conversion (DC) values of samples exposed to water bath are presented on the same time scale (circles)

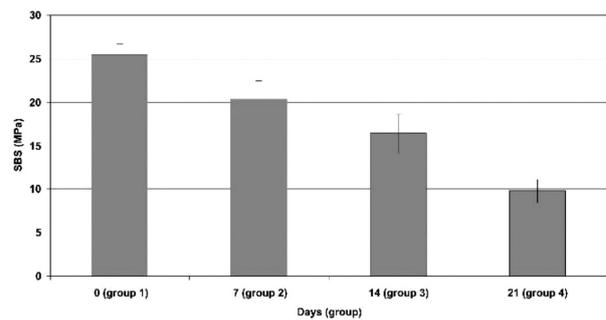


Figure 5: The Shear bond strength values of four groups of composite samples in different time intervals

of the samples. It was estimated that there is a statistically significant difference between the samples from group 1 to group 4 ($p = 0.001$). The post-hoc Bonferroni test confirmed there were statistically significant differences between group 1 with the saturated free radical concentration and group 3 ($p = 0.006$) and group 4 ($p = 0.001$), a statistically significant difference was also found between groups 2 and 4 ($p = 0.001$).

The Spearman correlation test showed that the correlation between the radical concentration and the shear bond strength was approaching statistical significance ($p = 0.051$)

3.4 Failure mode

All the samples of group 1 with a high concentration of free radicals failed cohesively in the underneath composite, while most of the samples (80 %) in group 4 failed adhesively. The failure modes in groups 2 and 3 had a progressive drop in the cohesive mode of failure from 80 % to 56 %.

4 DISCUSSION

During the adhesive cementation of the indirect restoration to the etched enamel and with IDS protected dentine, which is commonly 1 to 3 weeks after the initial appointment, we strive to achieve good bonding between the two composite materials. The micro-tensile bond strengths between the composite and the bur-cut enamel and dentine covered by different bonding agents or using different treatment times are in the range from 3.2 MPa to 49.5 MPa for the enamel and between 15.5 MPa and 63.1 MPa for the dentin.^{18–21} On the other hand, the bond strength between the two dental composite surfaces can be in the range between 5.7 MPa and 44.7 MPa, depending on how the surfaces are prepared and the application of different adhesion primers.^{10,22,23} It is assumed, but has never been directly proven, that the free radicals in the underneath layer are responsible for the successful bonding with the monomers from a subsequently applied composite layer.^{3,4,10}

For now it is not possible to isolate precise data for the concentration of the free radicals at the bonding

surface that are involved in the chemical bonding between two layers of composite.

Assuming that the free radicals in the thin superficial layer are responsible for bonding of new applied composite cement, we did not examine the creation and decay of free radicals in bulk samples, but in a 0.15-mm-thin layer of composite resin.

In view of the reported life span for the free radicals of up to 4–5 weeks, some authors indirectly presume that a period of 1–2 weeks would still provide a sufficient concentration of free radicals within the existing resin coating for a reliable bond with the newly applied layer.⁴ Other authors supposed that the free-radical decay is an even slower process and assumed the presence of free radicals that are suitable for a subsequent reaction in the composite substrate aged for up to 12 weeks.²⁴ However, a study employing EPR spectroscopy revealed that the half-life of the free radicals in bulk samples (25×2×2) mm of composites at 37 °C is 2–5 days.³

The observed discrepancy between our results regarding the time-dependent decay of free-radicals and those in the literature is understandable if we take into account that we have made measurements on 0.15-mm-thick samples, while other authors report the sample thickness to be 2–3 mm, and consequently the diffusion processes involved in the radical termination take a longer time.³

A supplementary experiment with Raman spectroscopy confirms that the polymerization process after the illumination continues and the polymer becomes stable after 48 h, which is in accordance with a previous study.²⁵ The DC sharply increased in the first 40 s of illumination until it reached a value of 47 %, when the polymerization slowed down owing to the low mobility of the monomers in a formed polymer network. Illumination for 120 s resulted in a DC increase to the value of 50 %. The diameter of the laser's focus spot sphere in the Raman experiment was estimated to be 10 micrometers. Therefore, both the DC and free-radical concentration measurements provided data from the thin layers. Free radicals are formed during the illumination, they undergo polymerization, at which time they are consumed very rapidly. With increasing DC values at higher illumination times and with the polymerization slowing down, the free-radicals are not consumed regularly and the concentration of free radicals is increasing until it saturates (**Figure 3**).

In our experiment the free-radical concentration decreased in the post-illumination period, while the DC continued to increase, which is in accordance with the findings of J. Leprince.²⁶ This is affected by the post polymerization and additionally with monomer elution as well as with hydrolytical degradation, at least in the topmost layers of the composites samples that were immersed in water after the illumination process.^{27,28}

Previous studies do not provide a direct explanation for the influence of the remaining free-radical concen-

tration in the aged composite about its bonding capability with freshly applied material.²⁴ Our study revealed that the high concentration of the free radicals in the underneath layer can provide reliable chemical bonding to the overlaid substrate. This enables both layers to act as a unit, which was confirmed by the 100 % cohesive failures of the samples from the first group.

This means that in the initial phase, the bonding between the composite and the composite cement, in particular, depends on the chemical interactions of the active free radicals of the two composite materials in contact. It could be expected that along with a recombination of free radicals, the capacity of the bonding between the two materials would decrease.

However, high shear-bond-strength measurements obtained in our experiment and the cohesive failure mode indicate that the concentration of free radicals has an impact on the SBS values only in the case of composite cement being applied to the freshly polymerised composite in the thin layer. Despite the relatively fast decrease of free-radical concentration (**Figure 4**), the SBS values in groups 2, 3 and 4 do not follow the dynamics of free-radical decay (**Figure 5**).

The radical concentration decreased to less than 10 % of the initial concentration after 3 d, while the number of cohesive failures after 7 d (group 2) decreased by only 20 %. We can conclude that the free radicals play an important role in improving the strength of the bonding in the initial phase of the layer formation, whereas later on, the bonding between the old and the new composite is also ensured by other mechanisms, e.g., an interpenetrating network.^{11,29}

The limitation of our study is that we used only one flow composite material and one composite cement. Maybe the radical decay in other brands of flow material is different and consequently the results would not be the same. However, we intentionally used the two materials produced by the same company to be as precise as possible in the results and conclusions. On the other hand, EPR spectroscopy detects the free radicals in the entire composite sample and not only at the bonding surface that is involved in the experiment.

5 CONCLUSIONS

The concentration of the free radicals in the fresh composite provides reliable chemical bonding to the newly applied layer. Measurements of the free-radical concentration in a thin layer of composite show a relative high decay rate; therefore, the influence of the underneath layer on the chemical bonding between two composite materials is high only in the initial phase after polymerization. The low free-radical concentration present within the composite substrate aged for 1, 2 and 3 weeks does not ensure chemical bonding to an overlaid, freshly applied composite.

Clinically acceptable bonding between the old and the new composite is ensured by other mechanisms that are less dependent on the free radicals in the underlying composite.

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