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EVALUATION OF FREE RADICAL CONCENTRATION IN SOME NEW DENTAL COMPOSITE MATERIALS BY ESR SPECTROSCOPY

DOINA PRODAN[a], LAURA SILAGHI-DUMITRESCU[a], PREJMEAN CRISTINA[a], RADU SILAGHI-DUMITRESCU[b], LAURA BOLOJAN[c], G. DAMIAN[c, *]

ABSTRACT. During polymerization of dimethacrylate monomers employed in dental materials, the gel effect leads to entrapment of radicals and unreacted monomers in the crosslinked network, affecting physico-mechanical properties and the biocompatibility. Reported here is a study of the effect of the resin composition, irradiation time and storage time of some new light-cured dental composites upon the free propagating radical concentration, using Electron Spin Resonance (ESR). Six new experimental dental light-cured composites based on the Bis-GMA monomer - 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl]-propane, on the corresponding Bis-GMA dimer, 2-hydroxyethyl methacrylate (HEMA) and on 1,6-Bis-[2-methacryloyloxyethoxycarbonyl-amino]-2,4,4-trmethylhexane (UDMA) have been employed, with three different photoinitiator systems. The hybrid filler consisted of quartz, strontium/zirconium glass and fluoro-hydroxyapatite. ESR signals developed under visible light irradiation during polymerization were measured, with intensities dependent on the time of irradiation. These signals decay very slowly in time – on the scale of days or longer.

Keywords: *Resin composites; ESR ; Free radicals*

INTRODUCTION

Light-cured resin composite materials are frequently used for direct restoration of anterior and posterior teeth [1,2,3], as sealants for the prophylaxis of caries with children [4], and in prosthetic dentistry for the preparation of composite veneers, inlays and onlays [5,6]. A crosslinked three-dimensional network is formed by the polymerization of the monomer mixtures existing in dental resin composites. During the polymerization of dimethacrylate monomers, the gel effect occurs, leading to the closing of radicals and unreacted

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[a] *"Raluca Ripan" Chemistry Research Institute, Str. Fantanele 30, RO-400294 Cluj-Napoca, "Babes-Bolyai" University, Romania*

[b] *Faculty of Chemistry and Chemical Engineering, Str. Arany Janos no.11, RO-400028 Cluj-Napoca, Babes-Bolyai University, Romania, rsilaghi@chem.ubbcluj.ro*

[c] *Faculty of Physics, Str. M.Kogalniceanu no.1, RO-400084, "Babes-Bolyai" University, Cluj-Napoca, Romania, grigore.damian@phys.ubbcluj.ro*

monomers in the crosslinked network [7]. The incomplete conversion of methacrylate groups affects the physico-mechanical properties and the biocompatibility of the dental composite materials [8]. The aim of the present work was to study the kinetics of free radicals formed as a result of the effect of the resin composition, irradiation time and storage time of some new light-cured dental composites, by Electron Spin Resonance (ESR) spectroscopy

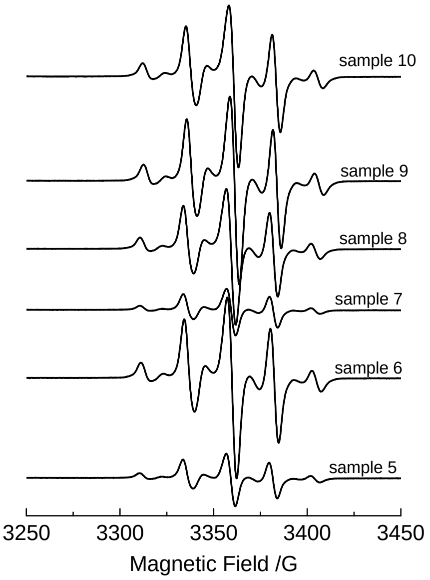

Figure 1. ESR spectra of free radicals after irradiation of the studied resin composite materials.

RESULTS AND DISCUSSION

Figure 1 shows ESR spectra measured immediately after polymerization by irradiation of the composite materials with visible light, cf. Materials and Methods. The nine line of ESR spectra are typicals, indicating the presence of polymer radicals of methacryl derivatives.

To characterize the kinetics of formation of radicals as function of the irradiation times, were determined relative concentrations of radicals for different periods of irradiation. The signal intensity, or the double integrated ESR spectrum, is proportional to the number of spins [9], and therefore can be used to estimate the relative concentration of the paramagnetic species.

Figure 2 shows the kinetic of radical formation, depending on the irradiation time. One may note that the intensity of the ESR signals is dependent on the time of irradiation and that this dependence shows saturation behavior at ~ 3 minutes.

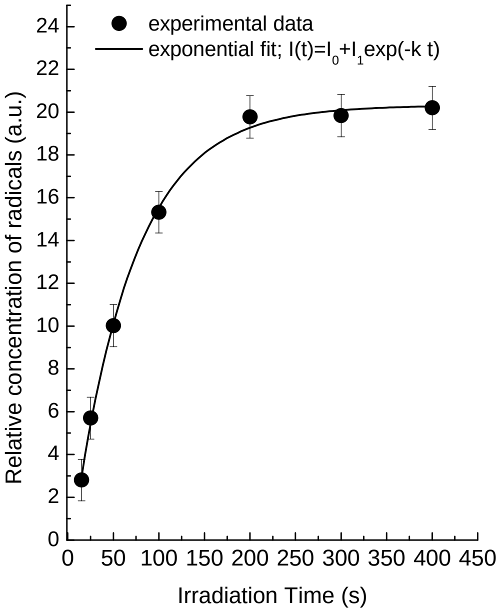

Figure 2. Dependence of relative signal intensity on the irradiation time.

In the case of samples 5 and 7 that contain the same CQ / DMAEM initiation system and different monomer mixtures, the initial relative free radicals concentrations were the lowest and presented closed values (6.5 for sample 7 and 6.2 for sample 5). For the other experimental samples (samples 5, 6, 7 and 8), the relative concentrations of free radicals were much higher, being situated in the range of 17 to 24 units of relative concentrations (17 arb. units for sample 8; 20 arb. units for sample 10; 22.5 arb. units for sample 6 and 24 arb. units for sample 9). Samples 6 and 8 contain the same initiation system -CQ / DMAEM / E-4-DMAB-, E-4-DMAB co-initiator being in addition to the samples 5 and 7. Samples 9 and 10 contain only CQ and E-4-DMAB as the initiator and co-initiator, respectively. Sample 8 and 10 contain UDMA in addition to monomer mixtures contained in sample 6 and 9.

The life-times of the radicals (time to reach half of the initial concentration) are consistent with different radical environments in the samples employed in the present study [8]. It is expected that the free radicals are closed in a highly cross-linked network having a long life-time. [2]. From the results obtained in the present study, it seems that CQ / DMAEM initiation system leads to the obtaining of the densest cross-linked network (the life-time of radicals are about 16 days). For the other samples, the life-time of radicals was in the range of 14 days (for sample 7) and 21 days (for sample 5).

From Figure 3 one can observe the general trend of decreasing the relative free radicals concentration in time, with different rates during samples aging, the concentration remaining constant after 60 days. The decay is bi-exponential.

CONCLUSIONS

Photopolymerization of dental resins at room temperature leads to the formation of long-life free radicals due to system vitrification. The kinetics of these free radicals was monitored by Electron Spin Resonance (ESR) spectroscopy. The ESR spectroscopy can provide new information which may lead to a better understanding of the phenomena existing in dental resins, like kinetics of generation and propagation of free radicals in the polymerization process and their stability.

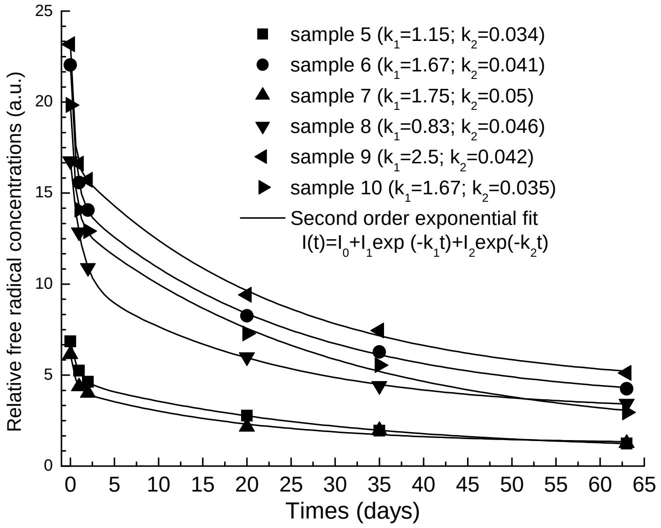

Figure 3. Dependence of relative signal intensity on the irradiation time.

Within the limits of the present experiments, the radical concentration depends primarily on the initiation system and secondly on the composition of the monomers used in experimental composites.

EXPERIMENTAL SECTION

Six new experimental dental light-cured composites were formulated using *two different monomer mixtures* based on Bis-GMA$_{336}$, 2-hydroxyethyl methacrylate (HEMA) and 1,6-Bis-[2-methacryloyloxyethoxycarbonyl-amino]-2,4,4-trmethylhexane (UDMA). Bis-GMA$_{336}$ was synthesized in our laboratory from the commercial epoxy resin D.E.R. 336 and contains the monomer 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propoxy)phenyl]-propane and the corresponding Bis-GMA dimmer [10]. *Three different photoinitiator systems* for free radical polymerization were used in the study based on the photosensitizer -camphorquinone (CQ)- in an amount of 0.5wt%, and two co-initiator reducing agents, dimethylaminoethyl methacrylate (DMAEM) in an amount of wt1% and ethyl 4-dimethylaminobenzoate (E-4-DMAB) in an amount of 1wt% related to the monomer mixtures. Butylated hydroxy toluene (BHT) was added as an antioxidant in a quantity of 650 ppm. The formulas of the dimethacrylic oligomers used in the experiments are presented in Figure 4:

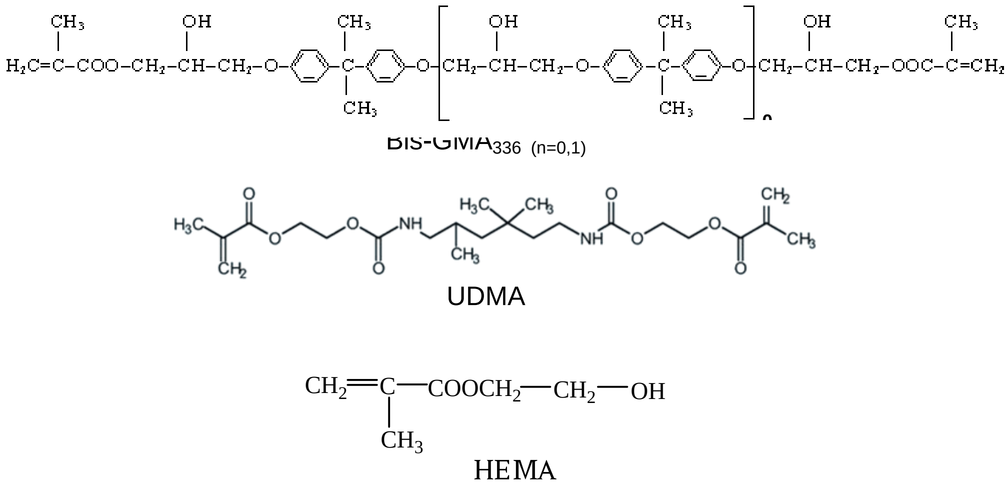

Figure 4. The chemical structures of methacrylate monomers used in the experiments

The hybrid filler (HF) was the same in all composite samples and consisted of quarts (40 wt %), strontium/zirconium glass (40 wt%), and fluoro-hydroxyapatite (20 wt%). The filler/monomer ratio was 4:1. The composition of the experimental dental light-cured composites are presented in Table 1.

The cured composite samples were obtained by exposing the paste composite samples to a visible radiation in the wavelength range of 400-500 nm. The radiation was generated by an Optilux dental lamp, produced by Demetron Research Corporation USA.

Table 1. Description of the samples examined in the present study

Monomer mixture + Hybrid filler / Initiation system	- Bis-GMA336 (12wt%) - HEMA (8wt%) + - Quartz (32wt%) - Sr/Zr glass (32wt%) - FHap (16wt%)	-Bis-GMA336 (7wt%) -UDMA (3wt%) -HEMA (10wt%) + - Quartz (32wt%) - Sr/Zr glass (32wt%) - FHap (16wt%)
-CQ - DMAEM	Sample 5	Sample 7

- CQ - - DMAEM - E-4-DMAB	Sample 6	Sample 8
- CQ - - E-4-DMAB	Sample 9	Sample 10

EPR spectra were recorded at room temperature with BRUKER-BIOSPIN EMX spectrometer operating at X-band (9-10 GHz). The EPR parameters were set at 100 KHz modulation frequency, microwave power 0.5 mW, modulation amplitude 3 G; time constant 2.56 ms; scan time 60 s; receiver gain 10^3. Each sample was weighed and the concentration of free radicals has been reported per 1mg of sample. The integral intensities of EPR spectra were obtained by evaluating their double integrals using the Origin 8 program.

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