



## Hydroxyl radical release from dental resins: Electron paramagnetic resonance evidence

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### ABSTRACT

It is well known that polymeric free radicals remain trapped inside dental resins for a long time after photopolymerization. Moreover, although these high molecular mass compounds have very limited mobility, there is evidence to suggest that they disappear progressively over time. The purpose of this study was to provide new experimental data to help understand this phenomenon. To determine whether low molecular mass free radicals are released by dental composites stored in hydrophilic media, we used electron paramagnetic resonance spectroscopy to perform spin-trapping experiments on experimental and commercial samples stored in ethanol. Under these conditions, ethoxy radicals were produced. Further experiments demonstrated that (1) hydroxyl radicals were released from the methacrylated resin and (2) they reacted with ethanol molecules to produce “secondary” ethoxy free radicals. In addition to the well-known monomer toxicity of methacrylated resins, we may have identified a new source of concern for these biomaterials.

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### 1. Introduction

Resin composites, made of inorganic fillers within an organic matrix, are widely used for dental restoration. The organic matrix is produced by a photoinitiated radical copolymerization of dimethacrylate monomers. Light induces cross-linking of the difunctional monomers, which progressively leads to the vitrification of the material. As a result, two kinds of free radical are trapped in the network: allylic and propagating radicals (Fig. 1) [1]. It is well known that these compounds can remain stable for several months in the polymer network [2–4]. Nevertheless, they disappear more or less rapidly, depending on the storage environment, until they reach undetectable levels on electron paramagnetic resonance (EPR) spectroscopy [5,6]. For instance, Leprince et al. [7] recently investigated the fate of the trapped free radicals in dental resins stored in water, air, oxygen or argon. They demonstrated that the rate of disappearance decreased in the following order: water > oxygen > air > argon.

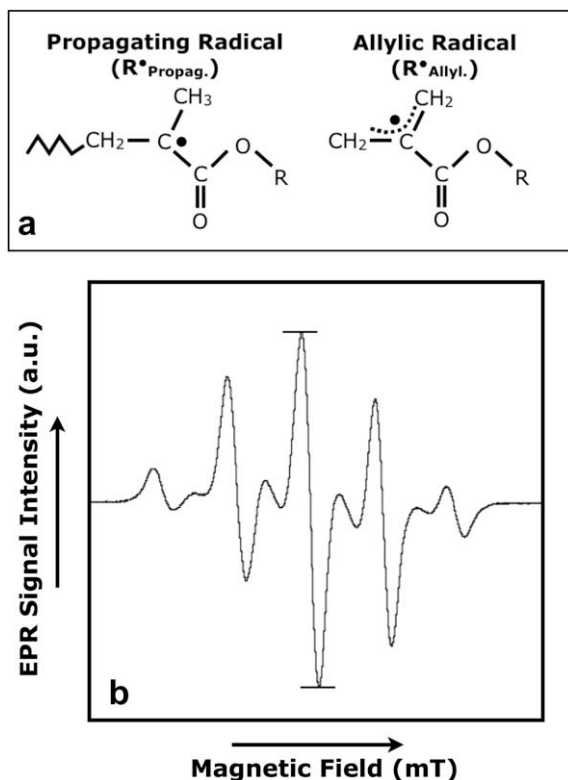
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Given the macromolecular dimensions of these trapped free radicals, their mobility into the polymeric network is strongly limited by entanglement and they cannot diffuse out of the resin. The decrease in trapped free radical concentration can, therefore, only be explained by radical reactions (distinct from typical methacrylate photopolymerization) occurring within the resin. It is then important, especially from a biocompatibility viewpoint, to know whether these reactions can produce and release mobile secondary free radicals into the environment. It has already been demonstrated that unconverted monomers are cytotoxic and can have harmful effects [8,9]. For instance, they can induce tooth pulp damage, mucosal irritation, contact dermatitis and allergic reactions [10]. Similarly, local release of free radicals could be another source of concern.

There are relatively few publications devoted to the stability of trapped free radicals in dental materials, and most of them have focused on the study of postpolymerization (or dark polymerization) [2,5,11,12]. The latter reaction occurs when the illumination is stopped and the resin stored in the dark. In this case, a slow decrease in the concentration of trapped free radicals can be observed due to termination phenomena (the rate of which depends on the cross-link density and on the storage temperature) associated with a certain increase in the degree of conversion [2,6].



**Fig. 1.** (a) Chemical structure of both trapped radical species (R represents either an end group or a connection to the network). (b) Nine-line EPR spectrum of the experimental resin after polymerization. Plain line on the spectrum corresponds to the position (allylic radical) where the intensity was measured for kinetic experiments.

In addition to postpolymerization effects, Leprince et al. studied the impact of the storage environment on the kinetics of the trapped free radicals [7]. Twenty-four hours after irradiation, oxidation was the main phenomenon involved in the decrease in radical concentration. Moreover, conditions influencing oxygen diffusion inside the polymer network (e.g. swelling in solvent) have an impact on radical kinetics. This effect of atmospheric oxygen was also noted by Pavlinec et al. [4]. Nevertheless, the exact mechanism involved has not yet been described. A generally accepted first step of the reaction leads to the formation of peroxy radicals (Eq. (1)):



Unfortunately, most studies have not detected these species by EPR spectroscopy despite the fact that evidence of the existence of peroxides has been published [7]. For example, Pavlinec et al. [4] recently noted, using chemiluminescence, that accumulation of these compounds occurred concomitantly with trapped free radical decay. Leprince et al. [7] hypothesized that low molecular mass radicals may terminate trapped species by recombination or disproportionation. In line with this hypothesis, Lee et al. [13,14] proposed that hydroxyl radicals could be released by hydroperoxidation of the methacrylated double bonds. If this hypothesis is valid, spin-trapping experiments are required to detect the hydroxyl radicals.

EPR spectroscopy and, more precisely, spin-trapping methods indeed enable the detection and identification of unstable free radicals [15,16]. This technique was first employed in the 1960s and has become increasingly popular because of the key role of radicals in many biological mechanisms and in deleterious processes in dis-

ease and ageing [17]. An unsaturated non-radical (diamagnetic) molecule, M, called the spin-trap, reacts with the unstable free radical, R<sup>•</sup>. The product, called the spin-adduct, M-R<sup>•</sup>, has a longer half-life than R<sup>•</sup> [18,19], allowing its detection by EPR. The hyperfine constants of the adducts (M-R<sup>•</sup>) are characteristic, enabling them to be identified. Nevertheless, due to the variable half-lives of spin-adducts, which depend on many parameters (nature of the trapped free radical and spin-traps, solvent, pH, temperature, etc.), detection may be more or less difficult. Typical spin-traps are nitroso compounds, like 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) or phenylbutylnitron (PBN). Currently, research is being conducted to synthesize new spin-traps with longer spin-adduct half-lives [20,21]. For instance, the spin-traps 5-ethoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (EMPO) and 5-diethoxyphosphoryl-5-methyl-1-pyrrolyne-*N*-oxide (DEPMPO) have been synthesized recently [22–25].

The objective of the present paper was to assess the potential release of free radicals from dental resin using spin-trapping methods. Ethanol was used as a solvent for immersion as it induces better swelling of methacrylated polymer than water, thus maximizing the diffusion of species in and out of the material. Because of the long half-lives of their spin-adducts, EMPO and DEPMPO spin-traps were chosen to characterize the free radicals released.

## 2. Materials and methods

### 2.1. Sample preparation

Experimental dental resins were prepared from a blend of bisphenol A glycidyl dimethacrylate (Bis-GMA, from Heraeus Kulzer, Dormagen, Germany) and triethylene glycol dimethacrylate (TEGDMA, from Sigma-Aldrich) in a 70:30 weight ratio. A photoinitiator system (1 wt.% of camphorquinone and tertiary amine obtained from Sigma-Aldrich) was added to initiate the polymerization. Point 4 (Kerr, Orange County, USA) was used as the commercial resin composite, which contains inorganic fillers. The resins (experimental or commercial) were inserted in moulds (7 mm long, 1 mm wide, 1 mm thick) and photopolymerized with a visible light device (Curing Light XL 3000, 3M-Espe, St. Paul, MN, USA). A constant intensity of 450 mW cm<sup>-2</sup> was applied for 40 s to one side of the samples. The mould allows not only the same sample geometry to be used for each experiment but also for the same amount of resin to be placed in the EPR cavity. These dimensions were chosen to ensure that the full area of the sample was covered by the diameter of the optic fibre of the lighting device.

### 2.2. EPR spectroscopy

The X-band EPR spectra were recorded at room temperature, using a Magnettech MINISCOPE MS200 spectrometer, equipped with a rectangular cavity (TE102). For kinetics experiments, the following instrument settings were applied: magnetic centre field, 336.7 mT; microwave frequency, 9.5 GHz; microwave power, 0.5 mW (23 dB); modulation frequency, 100 kHz; modulation amplitude, 0.1 mT; field sweep 19.8 mT, sweep time, 120 s; receiver gain, 100. For the spin-trapping experiments, all the parameters were identical except the sweep and centre of the magnetic field, which were adjusted to 9.8 and 335.6 mT, respectively. For all observations, the microwave irradiation power and the modulation amplitude were set to avoid signal saturation and were kept constant. Three samples were analysed for each experimental condition. Except for experiments with reduced oxygen pressure, the linewidth of the spectra was constant. The radical concentration

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