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ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY STUDIES OF COMPOMER TYPE DENTAL RESTORATIVES

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Key Words: Dental Restoratives, Compomers, Electron Spin Resonance Spectroscopy, Free Radical Decay Kinetics, Physical Properties

ABSTRACT

Electron spin resonance (ESR) spectroscopy was used to evaluate the curing kinetics of compomer type dental restoratives, determining rate constants and half-life of radicals. Physical strength measurements of the compomers were also determined for correlation with the ESR results. Compoglass (Ivoclar-Vivadent), Dyract (Dentsply), ANA (Nordiska) and Luxat (DMG) compomers were used in the study. Specimens, 3.2 mm diameter x 6.6 mm length, were cured in a plastic mold for 2 minutes, using an Elipar lamp. Immediately after curing, samples were examined by ESR, establishing time zero. The influence of conditioning at 37°C in water, 0.1M lactic acid, and 75% ethanol was examined. A Varian (E-9 X-band) ESR spectrometer was used to follow radical decay in all dental compomers studied. Peak intensities decrease during storage under dark conditions, accelerated by solution sorption which causes the matrix to swell, bringing about faster radical decay. Rate constants and half-lives of the radicals were calculated from the

average of $n=3$. Each system showed bi-exponential decay with one long lived half-life and one short lived half-life component. Radical decay rates for the four systems differ markedly, depending on their water sorption or conditioning method. Luxat and ANA were found by ESR and physical strength measurements to be structurally more homogeneous and water resistant than the other two compomers. Luxat exhibited the greatest half-life, i.e., longest radical decay profiles, on exposure to all conditioning methods, suggesting it would be the most stable compomer in dental applications. But, Luxat would be expected to release less fluoride in the oral cavity than Compoglass or Dyract.

INTRODUCTION

Dental Restoratives

Dental composites consist essentially of a mixture of monomers, usually dimethacrylates and an inert glass powder. Curing the composite simply joins the monomers into a crosslinked network, with the inert glass acting as a reinforcer. Glass-ionomers comprise an aqueous solution of an acid polymer and a reactive (basic), acid soluble glass. In this case, the polymer or copolymer are formed, but not crosslinked. Upon mixing, an acid-base reaction occurs in the glass-ionomer formulation, bringing about crosslinking of the polymer by salt-bridge formation and release of fluoride ions. Compomers contain monomers having both polymerizable methacrylate residues and acidic groups. The initial reaction occurs, as in a composite, by visible light initiated polymerization of the monomer(s), via the methacrylate groups. In the presence of water from the environment, a more limited glass-ionomer reaction also takes place, leading to some crosslinking via salt-bridge formation and the liberation of a substantially reduced amount of fluoride to the oral cavity. Compomers, or resin-modified glass ionomers, were developed to improve the physical properties and clinical handling of glass ionomers. Compomers can be designed to be light-activated and used as restoratives or liners [1].

Information about the nature of the radicals in the visible light curable dental restoratives may be derived from ESR spectra by analysis of the hyper-fine structure or shape of the absorption spectra. This arises because of the spread of the paired electron distribution over neighboring hydrogen atoms and subsequent coupling of the electron and proton magnetic moments.

ESR spectroscopy has been applied to the study of mechanisms and kinetics for a variety of polymer forming systems including photochemical polymerization and crosslinked acrylates or methacrylates [2]. Recent efforts have also focused on using spin probes to alter free radical polymerizations to produce narrow molecular weight resins [3, 4]. Polymers have also been functionalized with

spin probe residues to study such things as composite interfaces, water sorption, redox reaction in a matrix, estimation of microenvironmental rigidity in poly-electrolytes, and generation of materials with magnetic properties [5-7]. ESR spectroscopy has also been applied to a limited degree to study polymer blends, along with looking at non-invasive visualization of solvent swelling diffusion in solid polymers [8-11]. In the natural biomaterials area, some work has been accomplished on magnetic resonance imaging of biological specimens by EPR with nitroxide spin probes and characterization of irradiated and heated dental enamel [12,13]. Other studies have focused on looking at radical generation in light-cured dental composites and degradation of denture materials [14].

Using ESR, free radicals were identified in dental composites, along with providing additional information as follows: (1) the propagation of the conversion reaction as a result of exposure to light; (2) the time necessary for the decay of each type of radical; and (3) the variations with temperature and the effects of shattering on the materials under study. The presence of inorganic filling material slowed the process of polymerization, while it accelerated the decay of radicals. It was suggested that the nature of these processes depended on the composition of the base resin materials, whereas it did not depend on the sizes of the filler particles. Moreover, the complete propagation of the conversion reaction needed a period of light exposure greater than that currently suggested by the manufacturers. The structural stability of the composites was confirmed by both the long period of decay and the high temperatures needed to overcome the potential barrier for starting the radical decay process [15].

ESR was used to monitor and estimate the half-lives of propagating radicals in the visible light initiated polymerizations. The ESR spectrum measures the absorption of the microwave radiation energy which occurs when an unpaired electron undergoes a transition between its ground and excited state two energy levels (resonance condition). An ESR spectrum is a graphical representation of the intensity of the absorption at the resonance conditions as a function of the magnetic field intensity. ESR spectra are usually conventionally displayed as the derivative of the absorption curve [15].

ESR Theory

ESR Spectroscopy

ESR spectroscopy is based on the electron's characteristic of having a magnetic moment associated with its intrinsic spin angular momentum. The electrons thus behave as thin magnets.

Most organic molecules have an even number of electrons with coupled magnetic moments which cancel together in pairs, and, therefore, are non-magnetic.

ESR spectroscopy is an analytical tool which applies to molecular systems having either an odd number of electrons (free radicals) or more unpaired electrons. When free radicals are placed in a magnetic field, their energy is changed according to the orientation of the electron magnetic moment with respect to the field direction. According to quantum mechanics, the allowed orientations of the electron spin vector with respect to the field direction - *i.e.*, parallel and antiparallel orientations - resulted in two definite energy levels whose separation is proportional to the magnetic field intensity [15].

The ESR spectrum measures the absorption of the microwave radiation energy which occurs when a sample's free radicals undergo a transition between the two energy levels mentioned (resonance condition). An ESR spectrum is a graphical representation of the intensity of the absorption at the resonance condition as a function of the magnetic field intensity. ESR spectra are usually displayed as the derivative of the absorption curve. If H_0 and ν are, respectively, the magnetic field and the microwave frequency values at the resonance condition, then, for each radical in its environment, it is possible to define the magnetic parameter $g = h\nu / \beta H_0$, where h is the Planck constant and β is the so-called Bohr magneton [15].

The coupling between the spin of the unpaired electron and the spins of the magnetic nuclei, which are present in the free radicals, such as hydrogen nuclei, produces a further separation (hyperfine splitting) of the energy levels, the extent of hyperfine splitting is related to the interaction of the unpaired electron with the nuclei. Thus, each group of equivalent nuclei gives rise to a multiplet of lines which are separated from each other by the so-called "Coupling Constant = a ", measured in Gauss. The hyperfine splitting gives rise to an ESR spectrum with a pattern that depends on the types and numbers of nuclei involved. For the reasons noted, ESR spectroscopy provides a tool for the identification of free radicals and for the study of their structure [15]. ESR was found to be a valuable tool to characterize dental restoratives and to assist in the design of improved restoratives [16].

EXPERIMENTAL

Materials And Methods

Preparation of Samples and ESR Measurements

A group of commonly used or commercial, visible light-cured (VLC) compomers were selected for this study (Table 1).

Specimens were prepared with a diameter of 3.2 mm and 6.6 mm in height and light cured with an Elipar light source (ESPE Premier) in plastic molds. The

TABLE 1. Selected VLC Posterior Composites

Product Name	Class	Filler Type	Filler Wt %	Matrix Type	Producer (Batch #)
Dyract	Compules	Fluoro-silicate	N/A	a	Dentsply
Compoglass	CE 0047	Salanized mixed oxides Ba-fluorosilicate glass	N/A	b	Vivadent
Luxat	CE 0482	Ionomer glass	N/A	c	DMG
ANA Compomer	B1	Aluminum Silicate Barium Glass Pyrogenic Silicate	75	d	Nordiska Dental

a. Acid monomers and light curing polymers; b. BisGMA TEGDMA urethane dimethacrylate; c. Polymerizable oligo and polycarboxylic acids and other resins; d. Methacrylates light-curing polymers

cylindrical samples were irradiated in two directions for 2.0 minutes total to ensure the optimum polymerization of carbon-carbon double bonds throughout the specimens. All samples, after removal from the mold, were conditioned at 37°C in the wet condition. Solutions of distilled water, 0.1 M lactic acid, 0.1 M Tempol and 75% Ethanol were used. A mixture of 75% ethanol and water is considered to be an effective solvent for dental composites because it has a solubility parameter which is similar to that of the dimethacrylate resins used in these materials. Therefore, this co-solvent has been used in many studies to evaluate the long-term stability of dental composites during aging.

The acid-etching test involved immersion of the composite specimens at 37°C in 0.1 M lactic acid adjusted to pH (4.5) with KOH, since Cole *et al.* (1978) found such a pH value in plaque [17].

Measurements were taken with a Varian E-9 X-band ESR Spectrometer, modified with 13 field gradient coils in the rectangular TE 102 cavity. ESR spectroscopy instrument conditions for data collection in this work were 20.0 mW microwave power, 200 G scan range, 1.0 G modulation and scan rate time 2 minutes.

Each sample was taken out of the conditioning solutions, washed with distilled water, and dried. Samples were transferred into an NMR tube which was fixed firmly in an ESR cell, then the signal was monitored for a decrease in intensity. Initial measurements were taken over a time span of 2 minutes.

A spectrum was collected in a 2-minute scan, depending on the concentration of the radicals in the materials. A complete data set for one spectrum requires somewhere between 10-15 minutes to collect, providing data points which are easily collected at two to three times a day. The imaging technique is well described in the work which was done by Berliner [10, 12].

Mechanical Properties

Mechanical testing was performed in order to correlate the results of ESR with the results of mechanical tests over the same period of time.

Compressive Strength

The compressive strength of all compomers were determined by methods described in ADA Specification 27 for direct filling resins. Ten specimens ($n = 10$) of each material were prepared to dimensions of 3.2 mm dia. x 6.5 mm length using glass tubes. The ends of the specimens were machined flat and a load was applied utilizing a universal testing machine at a cross-head speed of 0.5 mm/min. The load to failure was recorded and the value of ultimate compressive strength calculated from the original cross-sectioned area of the sample using the following equation

$$CS = 4P \times 9.8 / \pi D^2$$

where P is the load, and D is the diameter.

All samples remained in distilled water at 37°C until the time of testing.

Flexural Strength

Flexural strength of compomers were determined by loading the flat ends of the specimens using a universal testing machine (Instron, Model 4204, Instron Corp., Canton, MA, USA) at a cross-head speed of 0.5 mm/min. Ten beam specimens 25 mm long x 2.09 mm wide x 2.34 mm thick of each compomer were prepared using Teflon molds. After insertion into the mold, the materials were compressed with a glass plate. The specimens were left to set in a humidior for 15 minutes, removed from their molds and then transferred to 37°C distilled water until the time of testing. The flexural strength was determined using a 3-point loading apparatus in an Instron machine. The compomer beams were laid horizontally between two parallel knife edges placed 20 mm apart. A progressively increasing

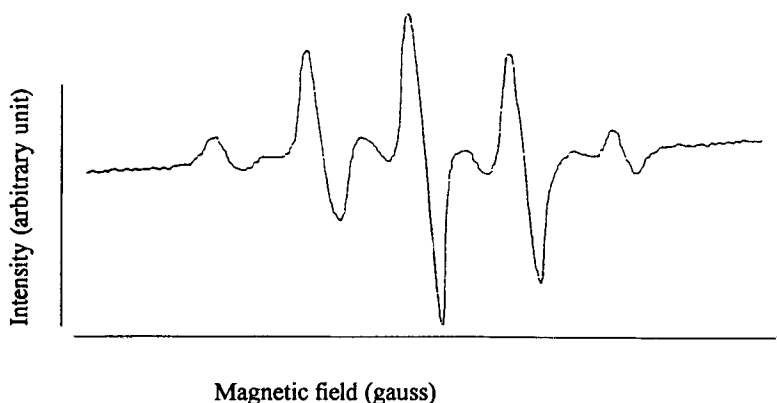


Figure 1. ESR (9-line) Spectrum of Visible Light-Cured Dental Materials.

load was applied at the midpoint between the knife edge supports, at a cross head speed of 0.5 mm/min. Specimens ($n = 10$) were tested after one day and 25 days ($n = 10$) storage in water. Flexural strength was calculated using the following equation:

$$\text{Flexural strength} = 3PL / 2bd^2$$

where P is the load at fracture, L is the distance between the two knife edges, b is the width of the specimen, and d is the depth of the specimen. An ANOVA was performed on the data for each property tested. For significant groups, Tukey's test was further performed at a rejection level of $p = 0.05$.

RESULTS AND DISCUSSION

Immediately after production, all samples (Dyract, Compoglass, Luxat and ANA compomers) showed a "9-line" spectrum (Figure 1).

The observed pattern was very similar to that analyzed by Ottavaini (15) and thus it is thought to be due to radicals such as:

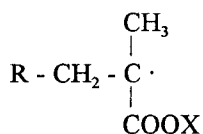


TABLE 2. Values of Rate Constants and Half-lives of the Commercial Dental Compomers in Solutions Water, 75% Ethanol and 0.1 M Lactic Acid

Material Name	Ave K_1	Ave K_2	t_1 $\frac{1}{2}$ (hrs)	t_2 $\frac{1}{2}$ (hrs)
Luxat in water	8.86×10^{-2}	2.62×10^{-3}	7.82	264.56
Compoglass in water	4.37×10^{-2}	2.68×10^{-3}	15.86	258.64
Dyract in water	4.93×10^{-2}	3.60×10^{-3}	14.60	192.54
ANA in water	2.51×10^{-2}	1.84×10^{-3}	27.62	376.71
Luxat in ethanol	1.21×10^{-1}	2.77×10^{-3}	5.73	250.23
Compoglass in ethanol	1.21×10^{-1}	1.56×10^{-3}	5.73	44.43
Dyract in ethanol	6.50×10^{-1}	6.7×10^{-3}	1.07	103.45
ANA in ethanol	4.68×10^{-1}	7.03×10^{-3}	1.48	98.5
Luxat in lactic acid	1.14×10^{-1}	3.33×10^{-3}	6.08	208.15
Compoglass in lactic acid	3.85×10^{-2}	5.39×10^{-3}	18.0	128.6
Dyract in lactic acid	6.50×10^{-1}	6.69×10^{-3}	1.07	103.6
ANA in lactic acid	4.15×10^{-1}	2.23×10^{-3}	1.54	310.83

where the nine-line splitting is due to the hyperfine interaction of the unpaired electron with the methyl and the methylene protons. This signal was identical for all compomers used. The intensity for the ESR signal was measured for each sample at different time intervals. Three samples were made for each compomer. The ESR peak intensity decreased during incubation under dark condition due to the monomer conversion in the deeper region and also due to the solution sorption which causes the matrix to swell and facilitate the polymerization in the dark. Tempol (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) was used as the known standard reference since the ESR spectrum of Tempol is well characterized.

Table 2 contains the values of rate constants and half-lives of the commercial dental compomers in solutions of 75% ethanol, 0.1 M lactic acid and water. The results were the averages of three runs for each material. In this table, all compomers show bi-exponential decay with one long lived half-life and one short-lived half-life component in each solution.

The bi-exponential decay equation has the formula:

$$Y = n \star \exp(-K_1 \star x) + (1 - n) \star \exp(-K_2 \star x)$$

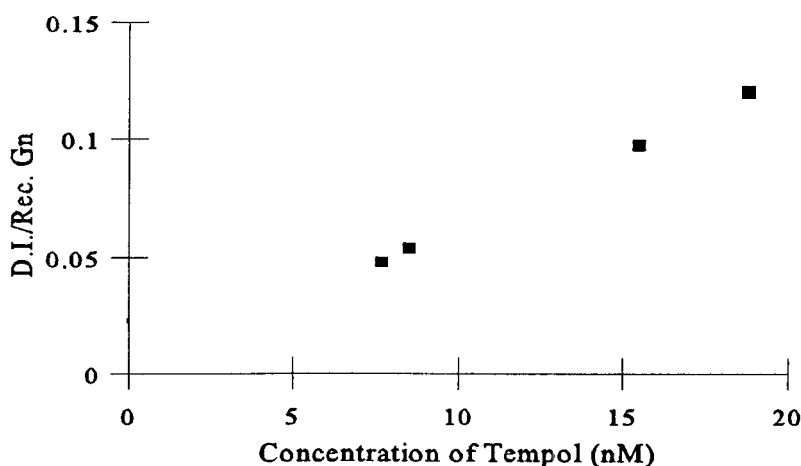


Figure 2. The Double Integrated ESR Signal Values vs Tempol Concentrations.

where n = number of free radicals of type K_1 , $(1 - n)$ = number of free radicals of type K_2 , x = time, Y = intensity of signals. K_1 and K_2 are the rate constants.

There is an effect of each solution on the lifetime of the free radicals. It is noted that two kinds of behavior exist. Samples in ethanol decayed faster than samples in lactic acid, while free radicals lived longer in samples immersed in water. This behavior is seen in all compomers. It may be noted that the long-lived component persist on the order of several days (half-life is typically 2-15 days). This implies that the free radicals existed for extended periods of time, which shows the effect of different soaking solutions on rate constants or half-lives. There is no real difference in short lived free radicals in all compomers. Compoglass has the shortest half-life among all other compomers in ethanol, while ANA compomer has the longest half-life in water and lactic acid. Ethanol seems to have a great effect on the structure of Compoglass, therefore, the half-life is the shortest. ANA compomer seems to have the greatest half-life in ethanol and water solutions. This may be due to enhanced hydrophobicity, filler-resin adhesion type and size of filler, etc. compared to the other compomers.

Initial free-radical concentrations were estimated for all compomers from the standard Tempol solutions. The double integrated ESR signal divided by the receiving gain values were plotted versus Tempol concentrations, showing a straight line (Figure 2). This plot was used to estimate the initial concentration of free radicals in all dental compomers (Table 2). The double integrated ESR signal value was divided by the receiving gain value, which is on the y-axis, e.g. 0.097 for

TABLE 3. Total Initial Concentrations of Free Radicals in All Materials Studied

Material	D.I/Rec. Gn	Total Initial No. of Spins (n moles)
Compoglass	0.054	8.50
Dyreact	0.097	15.50
Luxat	0.012	18.79
ANA	0.048	7.67

Double integration (D.I.), Receiver gain (Rec. Gn)

Dyreact, then extrapolating this value onto the line and coming down to the x-axis to find the initial concentration value which is 15.50 nm. The same procedure was used for all materials studied.

The values of the initial concentrations of free radicals in Compoglass, Dyreact, Luxat and ANA compomers were estimated and listed in Table 3 using Tempol as a concentration standard.

There is no pattern in the initial concentrations of free-radicals in commercial compomers when incubated with ethanol, lactic acid and water. It cannot be expected that these solutions will have any immediate effect on these materials since the short lived component is approximately 2-27 hours. Nevertheless, the initial concentration of free radicals in each species is high. The ESR signal decay over time in different solutions shows a decrease in intensity of the signal for all compomers. This decrease is due to the structural arrangements and also due to the radical decay or termination by atmospheric oxygen penetrating through the matrix-filler or the matrix itself, aided by diffusion enhanced swelling.

It is clear that free radicals were discovered which caused the defects in the polymeric matrix, and the inhomogeneity of the compomer structure. Some radicals are short-lived, but nevertheless, intense. Activity of the photopolymer is developed at elevated temperatures (exothermic reaction), and does not depend on the presence of any other catalyst, which suggests very strongly that highly active centers, such as free radicals, are embedded in the photopolymer prepared at room temperature and are accessible to monomer molecules under these conditions. A growing radical must, at some stage, become insoluble in the monomers and there will be a finite

TABLE 4. Physical Strengths of Commercial Compomers

Physical Strength	Compoglass	Dyract	Luxat	ANA
CS (MPa) (24 h)	189.71 (29.1)	210.22 (11.0)	239.41 (11.4)	235.31 (13.7)
(25 days)	145.71 (27.8)	202.07 (10.7)	222.11 (12.7)	214.12 (14.5)
FS (MPa) (24 h)	97.1 (8.4)	122.0 (7.2)	141.5 (3.1)	137.9 (2.6)
(25 days)	70.8 (11.2)	98.9 (9.7)	117.2 (4.2)	95.9 (3.4)
Mean values \pm SD ($p < 0.05$). CS: compressive strength, FS: flexural strength ($n = 10$)				

probability that the active end of the radical will become shielded by coiling of the molecule. Coalescence of polymer particles would be expected to greatly enhance the degree of shielding. Thus, polymer molecules containing free radicals are unable to react freely or at all with monomer for steric reasons (long-lived radicals).

The presence of different inorganic fillers in the compomers has an effect on the signal decay and caused it to be faster for all materials. Different soaking solutions showed different effect on the decay of the signal in all materials.

The compomer's physical strengths, which include compressive strengths and flexural strengths, were measured at times one day and 25 days in order to correlate the measurements of physical strengths with the decrease in ESR signal of all compomers studied. The compressive strengths and flexural strengths are summarized in Table 4. ESR signal of all materials studied has decreased over a time period of 25 days, due to the decrease in the number of free radicals trapped, which resulted in the decrease of the physical strengths. It can be seen that both strengths for Luxat and ANA were the highest among the four compomers. All compomers showed a decrease in both strengths over time, brought about by water induced degradation of the matrix-filler interface in the compomers.

CONCLUSION

Electron Spin Resonance (ESR) spectroscopy allowed free radicals to be identified in each compomer used. Also the radical decay rates of the four compomers were found to be different depending on their water sorption or conditioning methods. ANA and Luxat compomers were found by ESR and physical strength

measurements to be structurally more water resistance and releasing less fluoride in the oral cavity than Compoglass or Dyract. These results support the findings by Culbertson *et al.* [16] showing that ESR can be used as a tool to more fully characterize dental restoratives.

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