

## Analysis of the Photopolymerization Rate of Methacrylate Blends by Continuous Wave Free Precession NMR

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**Abstract:** Composite resins used in dentistry have an organic matrix based on a blend of dimethacrylate monomers like BisGMA and derivatives, UDMA and TEGDMA, which harden by free radical polymerization. The polymerization process can be initiated by visible light. The rate of polymerization reaction plays an important role in the clinical performance of resin restorations. Here, we used the continuous wave free precession (CWFP) technique to analyze the photopolymerization rate of dimethacrylate blends with millisecond time resolution. The liquid/solid ratio in the sample is related to the signal amplitude that depends on  $T_2/T_1$  ratio. The experiments were performed in a home built pulse NMR spectrometer based upon a bench-top Alnico V permanent magnet (0.17 T) and an Apollo transceiver (Tecmag). An Optilux 401 (Demetron) was used as a blue light source. All the methacrylate samples had the same composition, bisGMA+TEGDMA+UDMA +bisEMA, and different photoinitiators. The photoinitiators are as follows: sample a -PPD; sample b -MAPO and sample c -canthorquinone. Sample (c) has the highest polymerization rate, about 10s, sample (b) about 20s, and sample (c) about a few minutes. These results show that CWFP can be a useful technique to monitor photopolymerization of methacrylates in a low cost bench top spectrometer.

Composite resins used in dentistry as esthetic restorative materials consist of two principal components: organic matrix and inorganic fillers. Fillers, such as silanated glasses and colloidal silica, maximize mechanical and optical properties. The organic matrix is a blend of dimethacrylate monomers like BisGMA and derivatives, UDMA and TEGDMA, which harden the material by free radical addition polymerization. The polymerization process can be chemical or visible light-initiated with the latter component being preferable because of its time-controlled mechanism. The light cured matrix contains a photoinitiator system that absorbs light from a

light curing unit (LCU) to produce the primary radical species, which initiate the conversion of the monomers blend to a cross-linked network. Therefore, the rate of polymerization reaction plays an important role in clinical performance of resin restorations. However, there is very little information on the photopolymerization kinetics of dental resin formulations in the first few seconds of reaction. NMR is one of the techniques used to study this problem, including the use of  $^1\text{H}$  stray-field NMR imaging<sup>1</sup>.

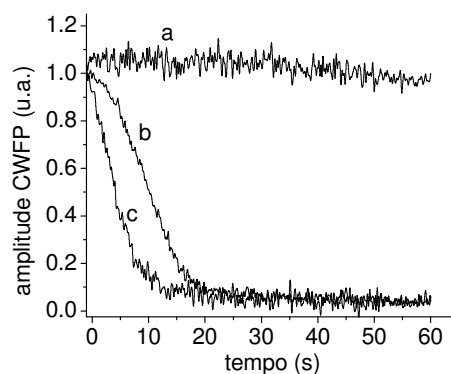
Here we used the continuous wave free precession (CWFP)<sup>2</sup> technique to analyze the photopolymerization rate of the dimethacrylate

blends with millisecond time resolution. In CWFP experiments, a train of pulses separated by a time interval  $T_r$ , shorter than  $T_2^*$ , was used. CWFP is a practical analytical tool for quantitative determinations and flow measurements<sup>2</sup> using a bench top NMR spectrometer. The CWFP sequence generates a continuous wave periodic signal that depends on the relaxation times  $T_1$  and  $T_2$ , tip angle  $\alpha$  and the precession angle  $\psi = \omega_0 T_r$ . When  $\alpha = \pi/2$  pulses and  $\psi = (2n+1)\pi$ , where  $n$  is an integer, the magnitudes of CWFP signal ( $S_0$ ) before and after the pulses become equal and dependent on  $(M_0 T_2 / T_1 + T_2)$ . By using this technique, the photopolymerization rates were measured with millisecond resolution ( $T_r = 300 \mu\text{s}$ ). The liquid/solid ratio in the sample is related to the signal amplitude that depends on the  $T_2/T_1$  ratio.

The experiments were performed in a home built pulse NMR spectrometer based upon a bench-top Alnico V permanent magnet with a field strength of 0.17 T. A single coil probe, holding samples 25 mm in diameter and 25 mm in height, was employed, leading to a signal decay with time constant  $T_2^* = 1\text{ms}$  caused by the inhomogeneity of the magnetic field over the sample volume. The electronic hardware consisted of an Apollo transceiver (Tecmag) Apollo, a Miteg AU1448 preamplifier and a gated AB type power amplifier. A continuous train of  $10 \mu\text{s}$   $\pi/2$  pulses separated by a time interval of  $T_r = 0.3\text{ms}$  and an acquisition time of 60s were employed. An external trigger was used to start the pulse sequence, and a time delay circuit (2 s) was used to open a diaphragm to initiate sample irradiation. The initial two seconds of the pulse sequence was necessary to reach the CWFP condition. An Optilux 401 (Demetron) was

used as a blue light source, filter band from 400-515nm, light guide of 13 mm diameter and power of  $400\text{mW}/\text{cm}^2$ . All the methacrylate samples have the same composition, *bis*GMA + TEGDMA + UDMA + *bis*EMA, and different photoinitiators. The photoinitiators are as follows: sample a –PPD; sample b –MAPO and sample c–canphorquinone. The results of CWFP analysis of the 3 samples with different initiators are in Figure 1.

As we can see in this figure, the rate of the polymerization of methacrylates samples can be monitored by the amplitude of CWFP signal. Sample (c) has the highest polymerization rate. Sample b polymerizes slower than sample a. Sample c has a very low polymerization rate of several minutes. In Figure 1 only one out of 64 points is used, because the process is slow compared to CWFP time resolution.



**Figure 1.** Amplitude of CWFP signal of the irradiated methacrylates samples with PPD (a), MAPO (b) and canphorquinone (c) photoinitiators.

These results show that CWFP can be a useful technique to monitor photopolymerization of methacrylates in a low cost bench top spectrometer.

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### References

1. T. G. Nunes, G. Guillot, S. G. Pereira, R. Pires. *J. Phys.D: Appl. Phys.* **35** (2002) 1251
2. R. B. V. Azeredo, L. A. Colnago, M. Engelsberg. *Anal. Chem.* **72** (2000) 2401; R. B. V. Azeredo, L. A. Colnago, A. A. Souza, M. Engelsberg, *Anal. Chim. Acta* **478** (2003) 313; R. B. V. Azeredo, M. Engelsberg, L. A. Colnago, *Phys.Rev.E* **64** (2001) 16309.