# Experimental report

10/02/2016

**Proposal:** **9-11-1714**

**Council:** 4/2014

**Title:** Investigating dental polymer structures of as a function of light-curing protocols using SANS

**Research area:** Chemistry

**This proposal is a new proposal**

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**Samples:**
d-TEGDMA / BisGMA
d-TEGDMA / UDMA

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D16 | 4 | 4 | 27/07/2015 | 31/07/2015 |

## Abstract:

Dimethacrylate resins are extensively used for dental filling materials but clinical performance is not ideal. The polymers are formed in-situ by photo-initiated free radical polymerisation to which the resultant physicochemical material properties are highly sensitive. Currently there is a drive towards rapid light curing protocols achieved through maximising light irradiance and modifications to photo-initiator chemistry. Rapid curing is however reported to impact on the tensile strength, toughness and hardness of these materials and whilst the effects on degree of monomer to polymer conversion have been extensively studied the impact of curing rate on its resultant polymer structure is unknown. The objective is to determine the cross-linked polymer structure of specific dental resins formulations as a function of the light-curing protocol (irradiance /photo-initator chemistry) employed. The internodal cross-linking distances will be measured using SANS providing insight into relative order correlated with the rate of polymerisation.

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| **ILL** | **No. 9-11-1714** | |
| **Experimental Report** | | |

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**Beamline** D16

## 1 - Abstract

Photo-initiated dental resin based composites (RBCs) are widely used in restorative dentistry as a filling material and a strong composite is required to reduce the likelihood of premature failure. The mechanical strength of an RBC is often extrapolated from its degree of polymerisation and a more converted material would be expected to display greater strength. Several studies though have shown that this interpretation is incomplete and that the rate at which the material is polymerised will also affect its mechanical properties. Accelerating polymerisation using high intensity light activation can impact on the tensile strength, toughness and hardness of an RBC[1-5]. Despite extensive mechanical characterisation of the cross-linked polymer the impact of curing rate on its resultant structure is unknown. The aim of this study is to determine the cross-linked polymer structure of specific dental resins as a function of the light-curing protocol employed. The inter-nodal cross-linking distances will be measured using SANS providing insight into relative order correlated with the rate of polymerisation used.

## 2 - Experiment details

Partially deuterated dental resin monomers commonly used as matrix components in composite filling materials have been synthesised from high purity precursors (Figure 1). Deuteration at the functional cross-linking sites allows inter-nodal cross-linking distances to be studied as shown below.

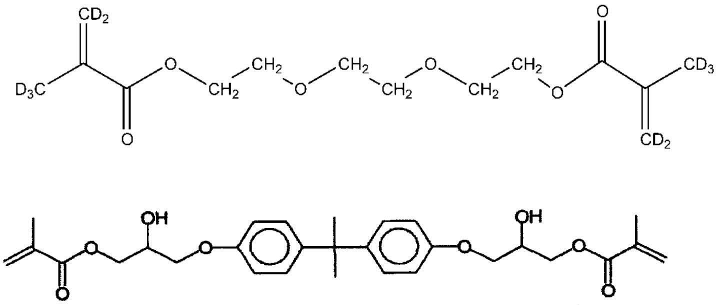

**Figure 1.** Chemical structures of partially deuterated TEGDMA (top) and hydrogenated Bis-GMA (bottom) monomers.

Dental resin monomer blends based on partially deuterated Tri-ethylene glycol dimethacrylate (d-TEGDMA) and hydrogenated Bisphenol A glycidyl methacrylate (Bis-GMA) have been produced in 60:40, 50:50 and 40:60 wt.% ratios. These blends were combined with a photo-initiator species of either 1 wt.% Camphorquinone (a slow initiator) or Lucirin TPO (a fast initiator) and photo-polymerised with two different powers of light whilst ensuring a matched total energy dose of 300mW/cm$^2$ for 60s (slow) and 3000mW/cm$^2$ for 6s (fast), to produce 1 mm thick disc shaped samples. An analogous series of RBCs were formulated by substituting d-TEGDMA with deuterated methyl methacrylate to understand conformational changes within this constituent monomer.

A third series comprised of a 60:40 wt.% blend of Bis-GMA/d-TEGDMA was combined with 8µm (diameter) silica particles to form a composite. The composite was combined with either 1 wt.% of Camphorquinone or Lucirin TPO and polymerised at either 300mW/cm$^2$ for 60s (slow) and 3000mW/cm$^2$ for 6s (fast).

SANS measurements were obtained using D16 over a $q$ range of 0.05-1.5 $Å^{-1}$, collected over three angle banks. Samples were enveloped within aluminium foil and mounted normal to the impinging neutrons for a run time of ~70 minutes per sample. To aid data analysis measurements were taken for direct beam, empty sample containers, water and a cadmium calibration standard to allow the scattering patterns to be corrected for background and normalisation effects. Data was reduced using the ILL in-house software LAMP (Large Array Manipulation Program) and subsequently fitted with a Gaussian model (Mantid software package, version 3.5) to determine peak positions and relative orders.

## 3 – Results

Our preliminary neutron scattering data obtained from D16 shows that polymerising clinically relevant dental resins (blends based on Bis-GMA and TEGDMA monomers) at extreme (fast and slow) rates of polymerisation results in different resultant polymer structures. Figure 2 shows the SANS profile of partially deuterated (within the methacrylate functional groups of the TEGDMA monomer) resin samples polymerised at high and low light intensities (fast and slow reaction rates) with the fast acting photo-initiator species TPO. The broad peak feature at $q$~0.6 $Å^{-1}$, attributed to the length of the TEGDMA monomer moves to lower $q$ following polymerisation, indicative of chain extension. A faster polymerisation rate, achieved through high light intensity, confers greater chain extension which is associated with polymerisation shrinkage (through the reduction of free volume). Additionally, systems polymerised rapidly typically exhibit ~ 10% less short range order relative to systems polymerised at slower rates.

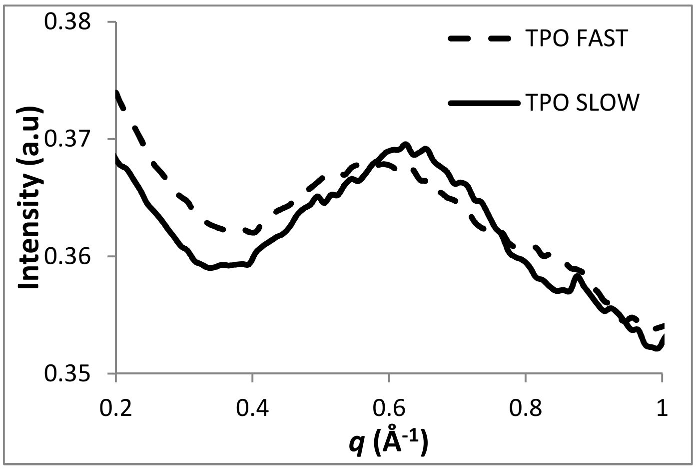

**Figure 2.** Neutron scattering data of a 60:40 (Bis-GMA/d-TEGDMA) blend containing Lucirin TPO (TPO) photo-initiator polymerised at fast and slow rates. The rapidly polymerised resin (broken line) displays a greater shift to lower $q$ *~0.55* $Å^{-1}$ than the slowly polymerised system ($q$*~0.6* $Å^{-1}$), implying chain extension within the deuterated TEGDMA monomer. Additionally, the 'fast' resin exhibits 10% less order relative to the 'slow' resin (obtained from FWHM values).

## 4 – Conclusions and Future work

For the first time we demonstrate that photo-polymerisation induces chain extension and modification to short range order in these materials. Accelerating polymerisation confers greater chain extension but reduced short range order in comparison to slowly polymerised systems. Chain extension may also act as a secondary mechanism facilitating volumetric shrinkage, by increasing the packing density, providing insight as to how similarly converted materials polymerised at different rates can demonstrate mechanical differences. The findings suggest that current interpretations of these materials which extrapolate mechanical properties from polymer conversion may be incomplete. Accelerating polymerisation can introduce structural differences which will dictate residual strain and may ultimately explain the discrepancies in the predictive modelling of the mechanical behaviour of these materials using conventional techniques.

## References

[1] Rueggeberg FA. Dent Mater. 2011;27:39-52. [2] Miyazaki M et al., Dent Mater. 1996; 12:328-32. [3] Dutra-Corrêa M et al., Minerva Stomatol. 2010; 59:645-51.[4] Ogunyinka A, et al., Dent Mater. 2007; 23:807-13. [5] Stewardson DA, et al., J Dent. 2004; 32:643-51.