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Experimental Report

Using structural correlations to inform the development of longer lasting dental restorations.

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Scientific background:

There is an increasing need to identify suitable replacements for mercury amalgam based dental filling materials, largely due to new European legislation governing the manufacture and disposal of mercury-based products[1]. The most promising alternatives are composite materials based on dimethacrylate polymer chemistry incorporating inorganic fillers. Following application to the prepared tooth surface these materials are 'demand set' by means of free radical polymerisation, stimulated by light excitation of a photo initiator dispersed within the resin matrix. Photo-polymerisation variables have been demonstrated to significantly impact on mechanical properties and clinical performance. Despite extensive mechanical characterisation of the cross-linked polymer the impact of curing rate on its resultant structure is unknown.

Following application to the prepared tooth surface dental resin composite materials are 'demand set' by means of free radical polymerisation, stimulated by light excitation of a photo initiator dispersed within the resin matrix. Currently most light curing protocols require 40 seconds or more of specified light wavelength exposure at intensities from 400 to 800mW/cm^2 per increment of material (up to 10 increments may be required per filling), to achieve the desired conversion of monomer to polymer[2,3]. Extensive research is currently being undertaken by academia and industry to develop shorter light curing protocols to reduce treatment times and reduce operator induced curing variability[2,3]. As a result, high intensity lights are now being advocated and brought to market which enable photo-polymerisation in as short a time as 3 seconds[3]. It is widely reported that accelerating polymerisation using high intensity light activation can impact on the tensile strength, toughness, hardness and degree of polymerisation shrinkage of these materials[4-7]. Despite extensive mechanical characterisation of the cross-linked polymer the impact of curing rate on its resultant structure is surprisingly unknown. We therefore plan to investigate the structure using small angle X-ray scattering.

Experiment:

Dental resin monomer blends based on Triethyleneglycol dimetharcylate (TEGDMA) (Figure 1a) and Bisphenol A glycidyl methacrylate (BisGMA) (Figure 1b) were prepared with varying wt.% ratios from 30:70 to 70:30. These blends were combined with photo-initiator species, 0.1% Camphorquinone ($C_{10}H_{14}O_2$) and photo-polymerised using different radiant exposures but ensuring matched total energy doses e.g. 3000mW/cm^2 for 10s, 300mW/cm^2 for 100s. SAXS measurements were acquired for the uncured monomers and cured specimens prepared at controlled time points prior to the experiment.

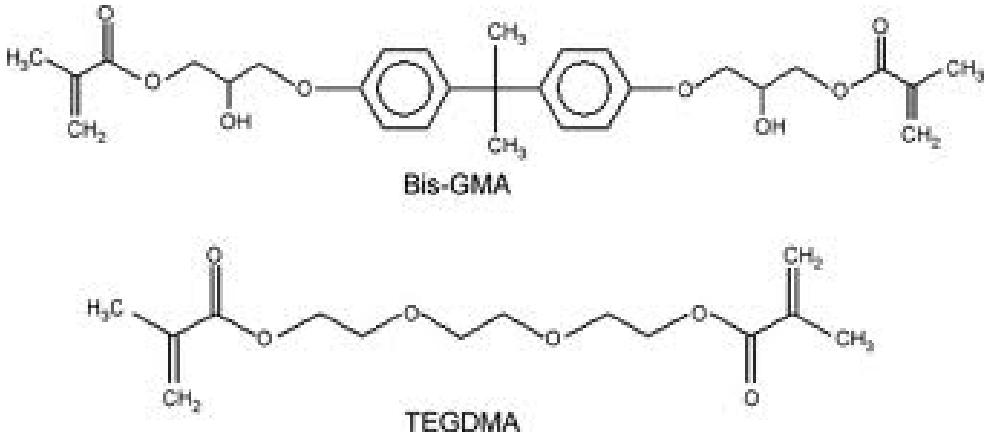

Figure 1. BisGMA and TEGDMA momoner structures.

Results:

The results showed a clear shift of the correlation peak to lower Q values during the photo-curing. The peak was also narrowed during the polymerisation indicating that the structure becomes less disordered. Preliminary time resolved kinetic studies were also undertaken. As shown in Figure 2 the polymer structure changes markedly after as little as 2 seconds photo-curing.

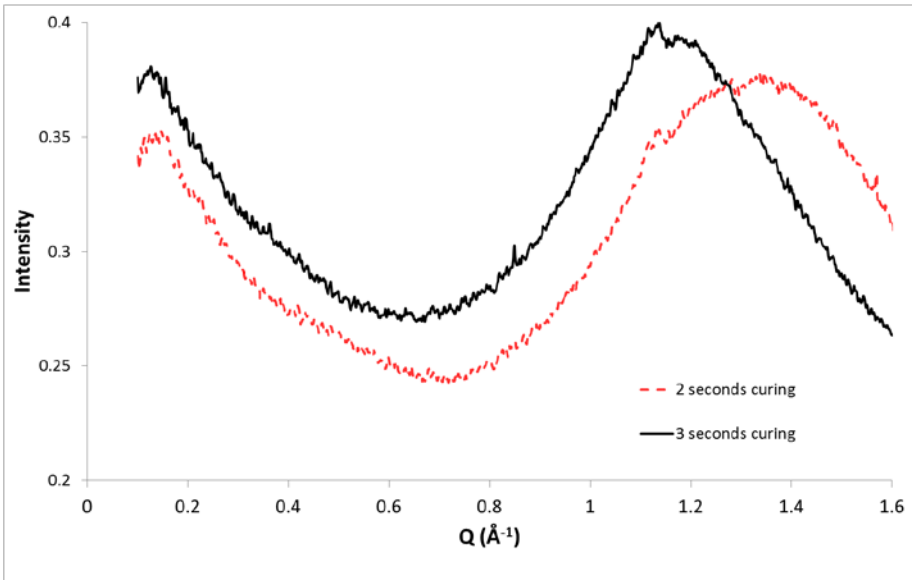

Figure 2: 60%wt hydrogenous Bis-GMA and 40%wt TEGDMA with 0.1 Camphorquinone photo-initiator. The broken (red) and solid (black) curve shows the structure after photo-curing for 2 and 3 seconds respectively.

We are currently undertaking the data analysis, correcting for incident intensity, background and absorption and normalising the intensity to water. Preliminary data fitting is being undertaken using a broad peak model.

References: [1] Ferracane JL. Dent Mater. 2011; 27:29-38. [2] Jiménez-Planas A, et al., Quintessence Int. 2008; 39:74-84. [3] Rueggeberg FA. Dent Mater. 2011;27:39-52. [4] Miyazaki M et al., Dent Mater. 1996; 12:328-32. [5] Dutra-Corrêa M et al., Minerva Stomatol. 2010; 59:645-51.[6] Ogunyinka A, et al., Dent Mater. 2007; 23:807-13. [7] Stewardson DA, et al., J Dent. 2004; 32:643-51. [8] Le prince et al., Dent Mater 2011;27: 157-164.