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Effects of filler type and content on mechanical properties of photopolymerizable composites measured across two-dimensional combinatorial arrays

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Abstract

Multicomponent formulations coupled with complex processing conditions govern the final properties of photopolymerizable dental composites. In this study, a single test substrate was fabricated to support multiple formulations with a gradient in degree of conversion (DC), allowing the evaluation of multiple processing conditions and formulations on one specimen. Mechanical properties and damage response were evaluated as a function of filler type/content and irradiation. DC, surface roughness, modulus, hardness, scratch deformation and cytotoxicity were quantified using techniques including near-infrared spectroscopy, laser confocal scanning microscopy, depth-sensing indentation, scratch testing and cell viability. Scratch parameters (depth, width, percent recovery) were correlated to composite modulus and hardness. Total filler content, nanofiller and irradiation time/intensity all affected the final properties, with the dominant factor for improved properties being a higher DC. This combinatorial platform accelerates the screening of dental composites through the direct comparison of properties and processing conditions across the same sample.
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1. Introduction

Dental composites are complex systems comprising a photopolymerizable binary or ternary resin mixture filled with inorganic particles. As such, a large number of chemical and processing parameters influence their properties [1]. For a given resin system, the size and concentration (loading) of the fillers used to reinforce the composite affect the final properties. The filler concentration is often dictated by the target application. For example, flowable dental adhesives are lightly filled, whereas composites for restoring posterior teeth are highly filled to withstand the greater forces of mastication. A high filler loading is advantageous because it leads to superior composite strength and reduced photopolymerization-induced shrinkage. The size of the filler particles also affects the composite properties. For instance, commercial dental composites are often filled with both micron-size and nano-size particles. Micron-size particles are used to increase filler content while retaining processability, while nanofillers are incorporated to increase wear resistance [1].

Dental composites must meet a stringent series of performance benchmarks to achieve clinical acceptance. Because of the complexity in the composite formulation, systematic variation of formulation parameters and subsequent screening of multiple properties on a large number of samples is time consuming, laborious and often impractical. In the most complete studies involving reaction kinetics, conversion, physical/mechanical properties and

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biocompatibility, only a single formulation is considered. Yet material and processing parameters are intertwined such that one formulation may exhibit weak performance improvements, while a slightly different formulation exhibits significant performance improvements. This complexity underscores the importance of screening a large number of parameters, as a single formulation that optimizes all properties often does not exist.

High-throughput and combinatorial (HT&C) methods using either continuous gradient or discrete array libraries have the advantages of faster data acquisition, wider examination of experimental variables, equal processing conditions for a given specimen, and greater experimental statistics over traditional one-at-a-time methods [2]. Material properties can be characterized and analyzed over a large parameter space by fabricating an array specimen varying in two material parameters. In addition, multiple chemical and physical characterization techniques may be employed on the same specimen to allow a thorough structure–property characterization. The ability to compare multiple properties on the same platform is especially suitable for photopolymerized dimethacrylate polymers, because the resulting material properties vary greatly depending on the sample preparation procedure. Preparing a series of systematically varied, individual samples for multiple material property characterization is a challenging task given the sensitivity of the photopolymerization process to changes in light intensity and sample geometry; thus, combinatorial approaches are advantageous for these materials.

Various fabrication and characterization tools for rapid measurement and analysis have been adapted for HT&C methods. Spectroscopy such as Fourier transform infrared (FTIR) spectroscopy, FTIR in reflectance mode (RM) [3], near-infrared (NIR) spectroscopy [4] and Raman [5] are ideal for determining chemical information. The surface morphology can be characterized by microscopy techniques including optical and confocal microscopy. In addition, depth-sensing indentation (DSI) testing or nanoindentation is well suited for mechanical property measurements [4,6–8] and has been demonstrated to be useful in the characterization of dental composites, ceramics and alloys [9,10]. Recently, the indenter probe has been used to produce well-controlled scratches with either a constant load or progressively increasing load (progressive-load scratch) with the resultant scratches characterized by confocal microscopy or light scattering [11,12]. The scratch resistance and polymer relaxations (elastic–plastic transition and scratch damage patterns) can provide additional insight into time- or strain-dependent material properties. For materials used in biomedical applications such as dental restorations, biocompatibility is another critical concern. HT&C methods have been shown to increase the throughput of bioassays [13] when characterizing biocompatibility of materials.

We have been utilizing HT&C methods to screen multiple properties of dental polymers. Our previous studies focused on two-dimensional (2-D) composition arrays and degree of conversion (DC) gradients of dental polymers using a monomer system consisting of binary mixtures of bisphenol A-glycidyl dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) [14]. We have also studied biocompatibilities of dental polymers [13,14] and composites [15] using 2-D platforms. In the current study, we investigated the effects of filler size and concentration on various chemical, physical and mechanical properties, in addition to biological properties. Cell studies were performed using a macrophage cell line, as macrophages are mediators of the inflammatory reaction and have been shown to be useful when evaluating the cellular responses to dental materials [16–18]. All measurements were performed on the same samples – the 2-D specimens – thus allowing direct comparison of the data. A suite of methods that includes NIR spectroscopy, laser scanning confocal microscopy (LSCM), DSI testing, scratch tests coupled to imaging, and bioassays modified specifically for combinatorial studies provide insight into the effects of composition/irradiation on properties. All of the properties examined have a critical impact on the clinical performance of dental composites.

2. Materials and methods

2.1. Materials

Resins BisGMA and TEGDMA were obtained from Esstech Inc. Photoinitiator system components, camphorquinone (CQ) and ethyl 4-*N*,*N*-dimethylaminobenzoate (4E), were purchased from Aldrich Corp. The SP 345 silane glass filler (SG, 0.70 μm average diameter) and fumed amorphous silica filler (OX50, 0.04 μm average diameter) were provided by the L.D. Caulk Company. Methacryloxypropyltrimethoxysilane (MPTMS) and *n*-octadecyltrimethoxysilane (OTMS) were purchased from Gelest, Inc. Cell culture reagents were purchased from Invitrogen Corp., unless otherwise noted. All reagents were used as received.

2.2. Composite preparation

BisGMA and TEGDMA (mass ratio = 50:50) were activated for blue light photopolymerization with 0.2% CQ and 0.8% 4E (by mass) and stored in the dark until use. The SG and OX50 fillers were mixed into the activated resin following the formulations shown in Table 1. The 2-D specimens consisted of a discrete array in composite formulation (individual stripes) along one axis with an orthogonal gradient in methacrylate conversion.

The specimens were fabricated by adapting procedures previously used for specimens of unfilled polymers [14]. Briefly, a sample mold was prepared using two glass slides (50 mm × 75 mm), a polyester release film and a poly(dimethylsiloxane) spacer (thickness ≈1.5 mm) with five channels (3 mm × 60 mm). The spacer was placed on top of a glass slide covered with a release film, and then