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Development of an oxirane/acrylate interpenetrating polymer network (IPN) resin system

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ABSTRACT

Objective. Develop a hydrophobic, degradation-resistant dental restorative based on an Oxirane-Acrylate IPN System (OASys) with low shrinkage-stress to substantially extend clinical lifetime.

Methods. Unfilled OASys blends were prepared using dipenta-erythritol-hexaacrylate (DPHA) and *p*-cycloaliphatic-diepoxide (EP5000). Varying proportions of camphorquinone/iodonium photoinitiator, with a co-reactant oligomeric-diol, served as the experimental curing system. The effects of oxirane-acrylate ratio on the degree-of-cure (Durometer-D hardness), hydrophobicity (contact angle), mechanical properties (3-point bending), near-infrared FTIR degree-of-conversion (DoC), polymerization shrinkage, and shrinkage stress were determined. 70:30 BisGMA:TEGDMA resin served as control.

Results. Oxirane tended to decrease hardness and increase hydrophobicity. 0:100, 25:75, 50:50 EP5000:DPHA are harder after 24 h than control. 75:25 and 100:0 EP5000:DPHA increased in hardness over 24 h, but were softer than control. All groups increased in contact angle over 24 h. After 24 h, 50:50, 75:25 and 0:100 EP5000:DPHA were more hydrophobic (~75–84°) than the control (~65°). Acrylate DoC was ~60% across all experimental groups. Initial oxirane conversion varied from ~42% in 100:0 EP5000:DPHA to ~82% 75:25 EP5000:DPHA. However, oxirane DoC increased for 100:0 EP5000:DPHA to ~73° over 24 h, demonstrating dark cure. Moduli and ultimate transverse strengths of OASys groups were higher than for 0:100 EP5000:DPHA, with 50:50 EP5000:DPHA having higher modulus than other experimental groups. However, the control had higher modulus and UTS than all experimental groups. Volumetric shrinkage averaged 7% for experimental groups, but stress decreased dramatically with increasing oxirane content.

Significance. Hydrophobic, low shrinkage-stress OASys resins are promising for development of composites that improve longevity and reduce the cost of dental care.

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1. Introduction

Despite numerous advances in restorative composite technology over the last 50 years, the current clinical survival of posterior composites has been reported to be between 55% and 95% over 5 years [1]. Most current dental composites are based on methacrylate chemistry, and factors for failure include excess polymerization shrinkage and shrinkage stress leading to marginal gap formation and degradation by hydrolysis, acids, bases, and esterase enzymes [2–5]. Bulk degradation of current composite materials is slow, as shown previously by abrasive wear [6,7]. Nevertheless, it can still contribute to reduction of material integrity over time.

Thus, the overall goal of this work is to develop a hydrophobic, degradation-resistant Oxirane/Acrylate interpenetrating polymer network restorative resin System (OASys) with decreased shrinkage stress and greatly enhanced clinical lifetime compared to current BisGMA-based restorative materials. Oxiranes, also known as epoxides, are cyclic ether compounds that are more hydrophobic than methacrylates and can be chosen not to contain ester linkages. They polymerize via a cationic ring-opening process that reduces polymerization shrinkage and can take place independently from, but simultaneously with, acrylic polymerization to form an interpenetrating polymer network (IPN). The cationic ring-opening polymerization is also much slower than the free-radical polymerization of methacrylates, and thus, will allow stress relaxation and further reduce polymerization shrinkage stress. Additionally, it is not susceptible to oxygen inhibition at the surface and so these resins should have a higher degree of monomer-to-polymer conversion (DoC) at the surface than acrylates and methacrylates, and further provide protection against water imbibition and degradation. However, they tend to be stickier to handle, and have slower cure rates and higher exothermic reactions than (meth)acrylates, making them less favorable for use in clinical dentistry.

Acrylates are chemically similar to methacrylates and follow a free radical polymerization pathway [8]. However, acrylates typically have a higher rate and degree of conversion than methacrylates. Higher DoC reduces the release of unreacted monomer and degradation byproducts during hydrolytic degradation, since longer polymer chains require greater cleavage to the point where degradation products are small enough to diffuse out of the polymer matrix. Thus, the greater the molecular weight, the more hydrolysis steps are needed to obtain soluble and diffusible degradation products, rendering them more stable and biocompatible [9]. Further, in OASys resins, acrylates will solidify within a clinically acceptable time while allowing the slower cationic polymerization to continue and reduce shrinkage stress. We anticipate that these characteristics of acrylates will offset their hydrolytic susceptibility and make it possible to develop a balance of properties that are favorable for improved durability and clinical properties. Additionally, the IPN structure would increase toughness, and further increase resin durability [10].

Previously, a novel 3-component photoinitiator system was reported by us [11,12]. The original intent of this initiator system was to reduce cured acrylic resin color and color shift. However, it also has the ability to cure *via* both free radical (acrylic) and cationic (oxirane) initiation [13]. Thus, we chose a combination of camphorquinone (CQ) together with an iodonium cationic compound well known as an epoxy initiator (OPPI, 4-octyloxyphenyliodonium hexafluroantimonate, GE 4792092C) as the two-component initiator for this study. The basicity of tertiary aliphatic amines in a 3-component photoinitiator system, such as DMAEMA (N,*N*-dimethylaminoethyl methacrylate), may quench the H^+ produced by the CQ-photosensitized iodonium salt and retard cationic initiation [14]. Thus, DMAEMA was excluded and was only used as a co-initiator with CQ in the BisGMA:TEGDMA (bisglycidyl dimethacrylate: triethylene glycol dimethacrylate) control resin. The CQ/OPPI combination produces twice the free radicals as CQ/DMAEMA-type initiators and simultaneously sensitizes and initiates oxirane polymerization.

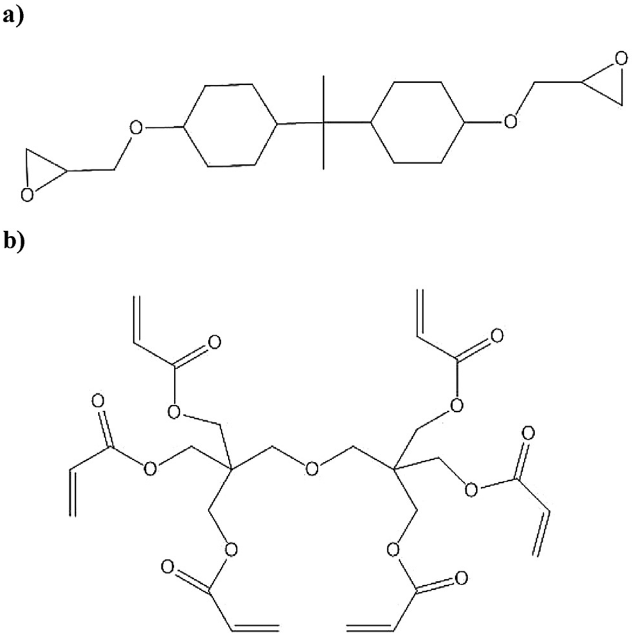

Fig. 1 – Chemical structure of monomers in the OASys resins. (a) *p*-Cycloaliphatic diepoxide (EPALLOY 5000^{TM} (EP5000)). (b) Dipenta erythritol hexaacrylate (DPHA).

The hypotheses to be tested were that increase in oxirane content increases hydrophobicity, and a well-formed interpenetrating polymer network has increased stress relaxation, along with acceptable physical and mechanical properties, compared to an oxirane or an acrylate homopolymer.

2. Material and methods

Varying concentrations of OPPI (Hampford Research, 2.2, 4.3, 8.24, and 15.2 wt.%), CQ (Sigma-Aldrich; 0.04, 0.095, 0.18, 0.36, and 0.79 wt.%), and a co-reactant oligomeric diol 250 Mn poly(tetrahydrofuran) (THF-250, BASF Corp.; 0.0, 1.14, 2.28, 4.56, 6.87, and 8.57 wt.%) were used with the following OASys blends of *p*-cycloaliphatic diepoxide (EPALLOY 5000^{TM}, EP5000, Fig. 1a, CVC Thermoset Specialties) and dipenta erythritol hexaacrylate (DPHA, Fig. 1b, Sigma-Aldrich): 0:100, 25:75, 50:50, 75:25, 100:0 EP5000:DPHA. The control consisted of a 70:30 BisGMA:TEGDMA monomer blend with an initiator system

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