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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-diepoxyde (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 24h than control. 75:25 and 100:0 EP5000:DPHA increased in hardness over 24h, but were softer than control. All groups increased in contact angle over 24h. After 24h, 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 24h, 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.

Keywords

Restorative resin; oxirane; cationic photoinitiation; acrylate; hydrophobicity; volumetric shrinkage; degree of conversion; interpenetrating network; shrinkage stress

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 hexafluoroantimonate, 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.

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™, EP5000, Figure 1a, CVC Thermoset Specialties) and dipenta erythritol hexaacrylate (DPHA, Figure 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 consisting of 1 wt.% CQ and 2 wt.% DMAEMA. Both control and experimental groups were each light-cured for 20 seconds on both sides (1000 mW/cm², Ultradent Valo® LED curing lamp, Ultradent Products, Inc.) to form 3/8" diameter by 1/16" thick specimens. Both the degree of cure (Durometer-D hardness) and hydrophobicity (contact angle measurements) were determined immediately after cure and 24 hours after storage in deionized water at 37°C. The second measurement was used to determine the effect of the slower "dark cure" component of the oxirane monomer. Samples that produced the hardest (best cured) specimens were further characterized for DoC (near infrared Fourier Transform Spectrometry, NIR), mechanical properties (3-pt bending), volumetric shrinkage (Acuvol, Bisco, Schaumburg, IL), and shrinkage stress (polymerization stress tester, Proto-tech, Portland, OR).

2.1 Degree of Cure (Durometer-D Hardness)

The Durometer (Pacific Transducer Corp, Los Angeles, CA) D-scale hardness of unfilled, cured specimens (n=5) was measured [15]. Three measurements were made on different areas of each specimen to verify cure uniformity.

2.2 Hydrophobicity (Contact Angle Measurements)

Contact angles were measured using a VCA1000 video contact angle instrument (AST Products, Billerica, MA). Images of three ~0.05 mL drops (one center, two on each edge) of

deionized water were captured by the camera 15 seconds after placement of water droplets on the specimen, and the angles were measured.

2.3 Degree of Monomer-Polymer Conversion (NIR)

DoC was determined in the near-infrared region using a Fourier Transform Infrared Spectrometer (NIR; Nicolet 6700 FT-IR) by measuring the disappearance of the C=C acrylate peak at $\sim 6165\text{ cm}^{-1}$ and the oxirane ring peak at $\sim 6080\text{ cm}^{-1}$ [12]. The DoC was calculated according to the following formula:

$$\text{DoC} = (1 - [\text{Abs cured}]/[\text{Abs uncured}]) \times 100$$

where Abs is the absorption peaks of the cured and uncured specimens, respectively [9].

2.4 Mechanical Properties (Three-Point Bending)

The control and various OASys blends were light cured into $40 \times 4 \times 2\text{ mm}^3$ bars and stored at 37.5°C in deionized water for 24 hours before they were cut into $3.54 \times 4 \times 2\text{ mm}^3$ bars ($n=15$). Modulus and ultimate transverse strength were then determined using a three-point bending test. An Instron/MTS 1125 ReNewTM universal mechanical test instrument was used with a three-point bending flexural test fixture at a crosshead speed of 1 mm/min , as previously described [16].

2.5 Polymerization Shrinkage (AcuVolTM)

Volumetric cure shrinkage was measured with the AcuVol II (Bisco, Schaumburg, IL). This instrument uses video imaging and calculates the percent volumetric shrinkage accompanying curing. Titanium dioxide pigment (0.01 wt.%) was incorporated into the monomers to ensure accurate identification of the droplet outline by the imaging software. Shrinkage was followed for 24 hours.

2.6 Shrinkage Stress (Proto-TechTM)

A polymerization stress tester (Proto-Tech, Portland, OR) was used to measure the shrinkage stress associated with photo curing. The force registered by the load cell was monitored for 24 hours, and the maximum-recorded force and the final force at 24 hours for each material was recorded [17, 18].

2.7 Statistical Analysis

All data was analyzed using analysis of variance (ANOVA) with Newman-Keuls *post hoc* test to determine significant differences between and among all groups at the $p < 0.05$ level.

3. RESULTS

3.1 Degree of Cure (Durometer-D Hardness)

The five resin blends made with the following co-reactant and initiator concentrations yielded the maximum hardness and hydrophobicity:

- 0:100 EP5000:DPHA - 1.19% THF250 + 4.3% OPPI + 0.09% CQ

- 25:75 EP5000:DPHA - 1.15% THF250 + 8.24% OPPI + 0.17% CQ
- 50:50 EP5000:DPHA - 2.29% THF250 + 8.24% OPPI + 0.17% CQ
- 75:25 EP5000:DPHA - 0.06% THF250 + 15.23% OPPI + 0.16% CQ
- 100:0 EP5000:DPHA - 2.1% THF250 + 15.16% OPPI + 0.63% CQ

Figure 2 shows the Durometer-D hardness of these unfilled resins. As oxirane concentration increases, hardness decreases with the 0:100 EP5000:DPHA group being the hardest. This demonstrates the difficulty in curing oxiranes. The 0:100, 25:75 and 50:50 EP5000:DPHA groups had significantly greater 24-hour hardness values than those of the BisGMA:TEGDMA control group (90 ± 2 , 89 ± 2 , 89 ± 1 DHN vs 88 ± 1 DHN, respectively). The 75:25 EP5000:DPHA (78 ± 5 DHN initially to 84 ± 1 DHN at 24 hours) and 100:0 EP5000:DPHA (74 ± 3 DHN initially to 82 ± 2 DHN at 24 hours) resins had significantly lower initial and 24-hour hardness values than those of the respective values for the control group. Surprisingly, a substantial dark cure was not detected between the initial and 24-hour hardness measurements in the 25:75 and 50:50 EP5000:DPHA groups that had lower oxirane content, but was clearly observable in the oxirane-only (100:0 EP5000:DPHA) group ($\sim 10.8\%$ increase in hardness, $p=0.000022$) and the 75:25 EP5000:DPHA group.

3.2 Hydrophobicity (Contact Angle Measurements)

Figure 3 shows the contact angles of water on the control and OASys resins. Hydrophobicity/contact angle significantly increases for all groups over 24 hours. It also tends to increase with increasing oxirane (EP5000) content. The 75:25 and 100:0 EP5000:DPHA groups were the most hydrophobic with both initial and 24-hour contact angles great than those of the control group ($64\pm 8^\circ$ initially to $84\pm 7^\circ$ after 24 hours and $65.5\pm 4^\circ$ initially to $80\pm 4^\circ$ after 24 hours vs. $53\pm 8^\circ$ initially to $65\pm 5^\circ$ after 24 hours, respectively, $p<0.0001$), while the 50:50 EP5000:DPHA group was significantly more hydrophobic than the control group only after 24 hours.

3.3 Degree of Monomer-Polymer Conversion (NIR)

Figure 4 shows the NIR DoC of the resins. Acrylate DoC was about 60%, but these are actually very high DoCs considering that DPHA is a multi-functional acrylate with five to six functional groups on each monomer. The control BisGMA:TEGDMA resin showed an initial conversion of $73.5\pm 0.007\%$ and a 24-hour conversion of $79.5\pm 0.008\%$. These high conversions are not surprising due to the fast cure of free-radical mediated polymerizations [19, 20]. The 50:50 and 75:25 EP5000:DPHA groups had significantly higher oxirane DoC than acrylate DoC, possibly demonstrating the development of a well-formed IPN. 100:0 EP5000:DPHA group demonstrated significant dark cure from $42\pm 0.04\%$ to $75\pm 0.006\%$ over 24 hours, an inherent feature of oxiranes. Control also had a significant conversion over 24 hr. However, this is surprising since other OASys groups showed an increase in hardness over 24 hours. The 25:75 EP5000:DPHA group had the lowest 24 hour oxirane DoC possibly indicating that the quick acrylate cure was immobilizing the oxirane monomers, and thus preventing them from polymerizing well.

3.4 Mechanical Properties (Three-Point Bending)

Figure 5 shows moduli and ultimate transverse strengths (UTS) of control and OASys resins. The control group has significantly higher modulus and UTS than all other groups. The 0:100 EP5000:DPHA group has significantly lower modulus and UTS than all other groups despite a DoC comparable to that of the control group. The effect of the interpenetrating network can be seen with the 50:50 group having the highest modulus ($2,104 \pm 67$ MPa) than all groups except the control group. However, 50:50 and 75:25 EP5000:DPHA groups were statistically similar. 25:75, 75:25, and 100:0 EP5000:DPHA groups were statistically similar moduli. Both the DPHA and Epalloy resins seem to be inherently weaker materials than the BisGMA:TEGDMA control.

3.5 Polymerization Volumetric Shrinkage (Acuvol™)

Figure 6 shows volumetric polymerization shrinkages of OASys and control resins ranging from 6–8%, but there was no statistical difference among the groups.

3.6 Shrinkage Stress (Proto-Tech™)

Figure 7 shows the polymerization shrinkage stress of OASys and control resins. The 0:100 and 25:75 EP5000:DPHA groups had significantly higher shrinkage stress than all other groups, including the control. However, as the oxirane content increased, shrinkage stress significantly decreased with the 100:0 EP5000:DPHA group having a shrinkage stress of only 0.03 ± 0.025 MPa/mm. The 50:50, 75:25 and 100:0 EP5000:DPHA groups had significantly lower shrinkage stress as compared to the control (0.6 ± 0.1 , 0.3 ± 0.1 , 0.03 ± 0.025 vs. 0.83 MPa/mm, respectively; ($p < 0.05$)).

4. DISCUSSION

A novel dental restorative resin system that forms an interpenetrating polymer network using oxirane and acrylic monomers is under development. The monomers cure *via* two independent mechanisms, a free radical and a cationic ring-opening mechanism, to create the interpenetrating network. This network has the potential of increasing mechanical properties and of taking advantage of various strengths of each of the monomer systems such as increased hydrophobicity, prevention of oxygen inhibition at the surface of the resin, increased resistance to degradation in the oral environment, and decreased volumetric shrinkage and shrinkage stress. As such, a model system was evaluated for degree of cure (Durometer D hardness and near infrared FTIR spectrometry), hydrophobicity (contact angle), mechanical properties (three-point bending test), and volumetric shrinkage and shrinkage-stress. These measurements were compared with a 70:30 BisGMA:TEGDMA control resin.

The 0:100, 25:75 and 50:50 EP5000:DPHA resins were harder (89–90 DHN) than the BisGMA:TEGDMA control (88 DHN). The 75:25 and 100:0 EP5000:DPHA groups demonstrated “dark” cure with a significant increase in 24-hour hardness.

OASys resins had varying DoCs depending on the ratio of oxirane to acrylate. While the acrylic DoCs stayed at about 60% conversion, both initially and after 24 hours. This is

actually very high since DPHA has a high degree of functionality [19]. The oxirane DoCs had a wider distribution. The 75:25 EP5000:DPHA group had the highest initial and 24-hr oxirane DoC indicating the most suitable monomer ratio for forming an IPN. The low 24-hour oxirane DoC in the 25:75 EP5000:DPHA group may indicate that with higher acrylate concentrations, the resin may be solidifying too quickly and retarding the slower development of oxirane cure and conversion. It is interesting that while the oxirane DoC was highest for the 75:25 and 100:0 EP5000:DPHA groups, their hardnesses were actually the lowest. This may simply be due to the fact that DPHA is more highly crosslinked than Epalloy 5000 due to its multifunctional nature, and thus, the higher the DPHA content, the higher its concentration on the surface. Regardless, the high conversion of both acrylate and oxirane is encouraging since that increases the probability that an interpenetrating network is forming [20].

Another benefit of having a high oxirane DoC is the increase in hydrophobicity compared to acrylic and methacrylic resins (Figure 3). Increasing oxirane concentration from 25% to 100% increases hydrophobicity from 71° to 84° after 24 hours water aging, which is 15° higher than that of the BisGMA:TEGDMA resin ($p < 0.05$). TEGDMA has been reported to have greater water absorption than BisGMA, up to 6.22 wt.% compared to BisGMA's 3.05 wt.% [21–23]. Since OASys resins are inherently more hydrophobic, they may better protect the resin from degradation in the oral environment. Of all the resins, the 75:25 EP5000:DPHA group had the highest contact angle of 84°.

Despite the increased hardness and good DoC, three-point bend tests show that OASys resins have lower elastic moduli and UTS than BisGMA:TEGDMA resins, whose composites are known for their high moduli and UTS (moduli 8–11 GPA and UTS 137–167 MPa) [22]. Nonetheless, these results do show the beneficial effect of having an IPN, as the 100% DPHA group had the lowest modulus and UTS (1279 MPa and 50 MPa, respectively). 100% EP5000 group had a modulus and UTS of 1810 MPa and 99 MPa, respectively, while the 50:50 EP5000:DPHA group had the highest modulus and comparable UTS (2104 MPa and 93 MPa, respectively). Thus, if monomers that produce higher strength polymers than those of DPHA or Epalloy 5000 were used, the OASys approach may be able to produce resins that are comparable and perhaps even superior to BisGMA:TEGDMA resins in mechanical properties.

Finally, both polymerization volumetric shrinkage and the shrinkage stress generated during polymerization were measured because, in dental restorations, methacrylate-based dental composite polymerization stresses have shown to lead to contractile forces on the tooth tissues and cause interfacial failures, bond failures, and progression of marginal gaps [25–26]. Modern methacrylate-based resins can have volumetric shrinkages of ~5% unfilled and 2–3% when filled [27–29]. Oxiranes should aid in stress relaxation over time *via* its ring-opening mechanism [20, 30]. This was verified in this work. While OASys resins had similar volumetric shrinkages to acrylates and methacrylates, they generated significantly less polymerization shrinkage stress, especially as the oxirane content increases. The decrease in shrinkage stress may be attributed to the lower modulus, however, the modulus data does not correlate with the shrinkage stress data with the 100:0 EP5000:DPHA group having relatively high modulus but the lowest shrinkage stress, and the 0:100 and 25:75

EP5000:DPHA groups having relatively low moduli but the highest shrinkage stresses. Rather, the results show that the oxirane content is the determining factor in shrinkage stress. An alternative explanation for decreased stress could be that the resin/testing surface interface fails at a low stress level due to poor bond formation. However, this was ruled out as no marginal gaps were observed following the stress test. Finally, since the OASys DoCs were very good, these results are encouraging.

The above results show that the OASys resins are promising. However, further work is required to improve mechanical properties and hydrophobicity and extend the investigation into filled systems. Unfilled resins have only limited use in dentistry, such as bonding adhesives and fissure sealants. Other applications require reinforcing filler to boost wear resistance and improve handling properties. Exploration of filled systems is presently in progress.

5. CONCLUSIONS

Current BisGMA-based composites are favored because of their physical appearance, ease of handling, and, most importantly, their mechanical properties. However, methacrylates generate significant polymerization shrinkage stress and are notably hydrophilic; they absorb water at a high rate, and the presence of ester bonds makes them subject to hydrolysis, ultimately shortening the lifetime of the restoration [3]. OASys resins using acrylate and oxiranes are being developed to replace current methacrylate-based resins. Our results demonstrate that OASys resins cure well, are more hydrophobic, and have lower shrinkage stress than BisGMA-based resins. However, they are mechanically weaker. Nevertheless, due to the hydrophobicity and extremely low shrinkage stress measured, the OASys approach warrants further study and development into filled systems, and to increase the proportion of oxirane in the IPN and increase resistance to hydrolytic degradation.

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a)

b)

Figure 1:
Chemical structure of monomers in the OASys resins. a) *p*-cycloaliphatic diepoxide (EPALLOY 5000™ (EP5000)). b) Dipenta erythritol hexaacrylate (DPHA).

Figure 2:
Durometer D-hardness of unfilled control (70:30 BisGMA/TEGDMA) and OASys resins. Same letters denote statistical equivalence between groups. Capital letters are for initial hardness values and small letters are for 24 hr data. * signify statistical differences between initial and 24-hour hardnesses within the same group.

Figure 3: Hydrophobicity (Contact Angle Measurements) of unfilled control (70:30 bisGMA:TEGDMA) and OASys resins. Same letters denote statistical equivalence between groups. Capital letters are for initial hardness values and small letters are for 24 hr data. * signify statistical differences between initial and 24-hour hardnesses within the same group.

Figure 4: Near Infrared Spectrometry. Degree of Monomer-to-Polymer Conversion of acrylates and oxiranes in OASys resins. Same letters denote statistical equivalence between groups. Capital letters are for initial hardness values and small letters are for 24 hr data. * signify statistical differences between initial and 24-hour hardnesses within the same group.

Figure 5: Elastic Modulus and ultimate transverse strength of unfilled BisGMA:TEGDMA control and OASys resins. Same letters denote statistical equivalence between groups. Capital letters are for UTS and small letters are for Moduli.

Figure 6:
Polymerization Shrinkage (Acuvol™) of unfilled BisGMA:TEGDMA control and OASys resins. (All groups are statically non-significant).

Figure 7:
Shrinkage Stress (Proto-Tech™) of unfilled BisGMA:TEGDMA control and OASys resins.
Same letters denote statistical equivalence between groups.