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Fracture Toughness Micromechanics by Energy Methods With a Photocure Fiber-Reinforced Composite

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Abstract

A fracture toughness analysis for discontinuous fiber reinforcement was evaluated as a function of fiber volume percent (V_f) using advanced flexural bend tests. Fully articulated fixtures with 40-mm spans were used to examine specimens ($2 \times 2 \times 50 \text{ mm}^3$) under conditions of Euler-type bending to reduce shearing effects. Testing for fracture toughness in standardized international units (kJ/m^2) using fundamental mechanics-of-materials energy methods by strain energy was then applied for assessment of resilience and work of fracture (WOF). Fracture toughness was also measured as strain energy release (SER_{IC}) for the condition of unstable fracture between peak load and 5% maximum deflection past peak load. Energies were calculated by numerical integration using the trapezoidal rule from the area under the load–deflection curve. Fracture depths were normalized using sample dimensions from microscopy imaging for a combined correlation matrix analysis of all mechanical test data. V_f significantly correlated with resilience, WOF, and SER_{IC} , but negatively correlated with degree of crack depth with $p < 0.0000005$. All measured interrelated properties also significantly correlated with one another ($p < 0.000001$). Significant fracture toughness differences between particulate-filled and fiber-reinforced composites began when adding fiber reinforcement at 10.3 V_f for resilience, 5.4 V_f for WOF, and 5.4 V_f for SER_{IC} ($p < 0.05$).

INTRODUCTION

The constituent geometry arrangements between fibers and polymer matrices have been presented in classical terms for the micromechanics of composites by the rule of mixtures [1–3]. Primarily, the composite modulus and strength have been evaluated by the rule of mixtures as a function of the fiber volume percent (V_f), including the fiber modulus or the fiber strength, respectively [1–3]. Modulus reflects elastic properties with minimal influence of the material flaws, but can also be used as an estimator for remaining composite strength

following matrix microcracking [4]. Regarding strength, materials rarely fail immediately at peak load, but rather following damage accumulation. As an alternative micromechanical consideration to modulus or strength for estimating bulk-material-breakdown properties, a mechanics-of-materials strain– energy methods analysis may provide insights about failure by using toughness measurements. Following damage build up, a critical flaw is stressed through a frontal plastic zone, resulting in rapid crack propagation [5, 6], where all proportions of the load– deflection curve can be measured with mechanics-of-materials energy methods for strain energy [7]. The elementary work (dU) done by a load (F) as the material is deflected by a unit distance (dx) is given by the equation

$$dU = F dx \quad (1)$$

The total work or strain energy is then

$$U = \int_0^{X_1} F dx \quad (2)$$

and equal to the area under the load– deflection curve between $X = 0$ and $X = X_1$. During brittle fracture with linear elastic deformation, the load– deflection curve is a straight line represented by $F = kX$, where k is the slope such that when substituting for F from Eq. 2

$$U = \int_0^{X_1} kX dx = 1/2 k X_1^2 \quad (3)$$

or

$$U = \frac{1}{2} F X \quad (4)$$

Strain– energy can thus typically be derived from the load– deflection curve for both elastic and plastic deformations. As an extension of the customary V_f micromechanics for strength or modulus, interpretations for the properties of fracture toughness as energy released or adsorbed per unit area or volume of specimen [5–7] should also be included. Fracture toughness is then defined most conventionally by traditional standardized texts for static low-strain-rate work of fracture (WOF), but can also be measured through static resilience, static strain energy release rate, and also high-strain rate impact strength in standard international (SI) units of kJ/m^2 [7–12]. SI units using Newton and millimeter data are conveniently produced during static testing with the force and cross-sectional sample dimensions to provide common units for strength in megapascals, in addition to the load integrated through a distance, to give toughness units in kilojoules per square meter.

When considering fibers, reinforced composites fail by complicated processes [1, 4, 6, 10–13]. Crack propagation resistance or fracture toughness for fiber reinforcement can be associated with polymer matrix microcracking, fiber debonding with the matrix, fiber breakage, fiber frictional pull-out, and fiber bridging [1, 4, 6, 10–13], which should be evaluated through a modified rule-of-mixtures analysis, considering the dominant function of V_f . Also, during debonding with fiber-reinforced composites, cracks tend to deflect by propagating down the fiber axis, so that fracture does not immediately proceed through the

material [1, 6, 10–13], which can further be evaluated through a rule of mixtures, considering the most important V_f contribution.

In view of the growing importance of smaller and thinner components and fiber-reinforced composites where toughness becomes an essential property specific to the control of fracture crack propagation, mechanics-of-materials strain–energy methods for bulk material properties were explored. Given that mechanical energy is a force relationship through a distance, using joule = (newton)(meter), then toughness values as kJ/m^2 for sample cross-sectional areas can be determined using the load–deflection curve, which has been commonly reported as resilience or WOF [6–12]. Moreover, owing to computer spreadsheet technology, toughness energy values can be readily calculated from the load–deflection plot using numerical integration [14]. Integration was done by summing the area under the curve between successive load/deflection data points consecutively. A polygon quadrilateral with two parallel sides is a trapezoid [10, 14] whereby

$$\text{Area} = \sum \frac{1}{2} (\text{base} + \text{top}) (\text{height}) \quad (5)$$

Parallel sides from the load–deflection curve thus represent successive force values, and the height is the deflection between corresponding data points. The convenience of energy calculations for toughness results were subsequently afforded directly from load–deflection data, without the need for additional expensive mechanical integrators, costly software, or time consuming graph paper calibrating, cutting, and weighing [10–12, 15]. The intention then was to provide convenient reproducible test results that represent bulk material fracture toughness properties for routine comparisons during research and development of a new discontinuous photocure fiber-reinforced composite [10].

To account for lateral crack propagation and high energy consumption in ductile fiber-reinforced composites, the area under the load–deflection curve from peak load to maximum 5% deflection past the peak force was considered [10]. The study of crack propagation could be investigated in relation to specimen deflection and the energy integrated beyond maximum peak or critical (C) load, where unstable damage initially occurs as critical strain energy release (SER_c) [10]. Toughness values as SER_c could be associated with critical strain energy release rate (G_c), which is really a true toughness value expressed in SI units of kJ/m^2 [10]. G_c was originally defined, following Griffith's criterion for unstable crack propagation, as the energy released when atomic bonds break to form a crack and grow new fracture surfaces [16–18]. Free unpaired electrons can be shown to form when atomic bonds are stretched [18], as possible disruptive potential energy available for fracture at critical load that might include other unstable, deformed electron orbitals. Griffith brittle failure only requires disruption of the organized interatomic bond forces on either side of the crack, which can be produced from the stored energy in the sample at fracture [16, 17]. Since then, G_c has been defined in many different ways to produce some uncertainty with terminology [17, 18]. However, Griffith theory cannot be used to explain ductile fracture that requires external forces to produce plastic deformation to continue crack propagation [16]. Subsequently, G_c was defined as the energy per unit increase in fracture crack surface area, and could be viewed as work in terms of displacements from both

loading forces or reductions for each unit increase in crack length [5]. In addition to brittle Griffith criteria, bulk comparisons for ductile fracture with plastic deformation were necessarily required for fiber-reinforced composites. Consequently, methods were developed to measure strain energy following maximum load and load reductions with continued strain during crack propagation over a fixed deflection as SER_c [10].

A more important objective was to present a new advancement in photocure polymer composites related to ongoing research and product development [10–12]. The United States Department of Energy had previously independently evaluated and mechanically validated improvements that included WOF and high strain-rate Izod fracture, following addition of 3.0 mm quartz fibers at 35 wt% to particulate-filled dental composites [11, 12]. During related testing that examined addition of increasing fiber lengths from 0.5 to 6.0 mm at 30 wt% to a photocure resin composited with 3M Corporation zirconia silicate particulate, fracture toughness measured by resilience, WOF, and SER_{IC} increased 6.5×, 6.7× and 67× respectively [10]. An advanced fiber-reinforced photocure vinyl ester composite is now under development with the intent to replace existing dental filling materials [10–12] and as a related material to improve cranio-maxillo-facial medical/dental devices and materials [10]. The fiber-reinforced molding compound is fundamentally a high-strength adhesive that bonds to complex curved spaces [10]. Photocuring can even be pulsed in low-second time intervals, and incrementally bonded [10] to prevent tissue “burning” from polymerization exotherms experienced over the brain during cranioplasty surgical procedures, using current chemical cure acrylics [19, 20]. Resin preimpregnation of the composite fibers and particulate, normally done under vacuum manufacturing conditions, also eliminates mixing needed onsite with chemical cure polymers, which produces numerous voids [21].

The vinyl ester resin was the culmination of over 30 years of dental chemistry development to produce nonthermal ambient-cure polymers [22–24]. Initial work started with tertiary amine redox couples for acrylic in Germany in the 1930s [22] and the epoxy resin development concurrently by De Trey Freres in Switzerland [23]. The final breakthrough for vinyl ester resin was produced at the National Institute of Standards and Technology through the American Dental Association in the late 1950s and early 1960s [24]. All dental composites now in fact are both styrene-free and methylmethacrylate-free, using diluent monomers designed to crosslink the vinyl ester dimethacrylate end groups. Current dental particulate-filled composites suffer from low mechanical properties that include toughness [10–12, 25, 26]. Toughness has been recognized as an important property related to the control of crack propagation [1, 6] and, similarly, for brittle particulate-filled composites that are often related to marginal chipping [26]. Surface roughness with low flow cleansing areas are then associated with increased recurrent decay rates [27]. The photocure fiber-reinforced composite research and development was further directed toward microelectronic encapsulants, providing low thermal processing conditions in addition to rapid field repair applications, with low external energy requirements.

To enhance mechanical properties, silanated pure quartz 99.99% silica fibers preimpregnated with a photocure vinyl ester resin system provided an exceptional reinforcement opportunity for particulate-filled photocured composites [10–12]. Pure quartz 99.99% silica fibers could provide maximum interfacial bonding conditions for functional

organosilane coupling with the vinyl ester photocure resin system, to maximize mechanical stress transfer across the fiber to matrix interface [28, 29]. The organosilane coupled quartz fibers with virtually no lattice structure impurities could further supply hydrophobic chemical resistance and thereby almost zero water solubility [28–30].

Discontinuous fiber-reinforced composites facilitate the molding of intricate geometric parts, and practically use fibers well above the critical aspect ratio (L_c/d) to ensure stress transfer between the fibers and the matrix [1, 31, 32]. With regard to successful polymer/fiber shear bond strengths, vinyl ester with unsaturated polyester composites are a major class of polymer materials that enjoy a worldwide market with ~4.4 billion pounds produced annually [33]. Owing to the associated large research activity, L_c/d s for silica-based fibers in a vinyl ester polymer have previously been estimated to be about 46–65 [10, 11, 34–36]. Stress transfer has been theoretically modeled, whereby fiber strengths are not expected to contribute to a composite before $2 L_c$ [37]. In addition, mechanical properties have been theoretically shown to plateau for fiber lengths at about 4–5 L_c [10, 38, 39]. Therefore, to investigate basic toughness mechanical properties, 3.0 mm length, 9- μ m diameter high-purity (99.99% silica) quartz fibers, approximately ~six times above the critical length (L_c), were incorporated in a photocure vinyl ester molding compound.

In addition, fracture toughness of photocure composites can be mechanically evaluated without thermal residual cure stresses that could influence microcracking in relation to test results [1, 40]. The photocure system under research and product development uses safer visible light rather than ultraviolet (UV) light. Although UV energy is generally used for thin coatings [40], longer wavelength visible-light photocuring with a complementary redox curing agent system provides depth of cures much deeper than UV [41], to facilitate curing of fiber-reinforced composites. Also UV fiber-reinforced composites for structural applications cure in times which are measured in minutes [42] compared to visible-light curing times that are measured in 10s of seconds [41].

The fracture micromechanics can subsequently be studied during research and development at varying V_{fs} related to system toughness, so that defects emphasized during plastic deformation can be minimized. In order to reduce error during mechanical testing and in particular sample defects that are accentuated during plastic deformation, an advanced test design was employed. Small sample sizes generally produce higher mechanical properties because of a lower concentration of defects [1], which can be easily accommodated by flexural testing. According to standards for advanced ceramics ASTM C 1161–94, fully articulated flexural bend fixtures have been shown to reduce error associated with sample parallelism inaccuracies [43]. Four-point testing has been recommended by experts in ceramic analysis in order to stress a larger amount of material relative to three-point type testing [43, 44], which becomes important for evaluation during research and development. However, three-point testing produces less shearing error and typically may give results 15% higher than four-point testing [44]. Also, an extended span length to sample depth ratio of at least 16 per ASTM D 6272–00 standard for polymers (reinforced) has been recommended to reduce shearing effects through Euler-type bending conditions [45]. In fact, a span to depth ratio of 20 has been recommended for fiber-reinforced composites that are

more susceptible to shear error [46, 47], and more as anisotropy increases according to ASTM D 6272–00.

Because of the interest in critical stress intensity factor (K_{IC}) testing, relative merits regarding bulk material strain– energy methods for V_f composite testing were considered. K_{IC} has been advocated through many different configurations with a wealth of empirical formulas that include numerous flexural or bend testing as a form of “fracture toughness” measured in $\text{MPa m}^{1/2}$ [5, 6]. The variety of test methods associated with uncertainty in terminology [18] and producing conflicting, contradictory results suggested that K_{IC} was a specific comparative test option and not a true bulk material property [46–48]. The National Academy of Sciences through an important ceramics materials advisory board on high-temperature engines has even requested that limitations should be imposed on reporting K_{IC} results [48]. K_{IC} has been considered not to be a material constant under certain conditions that can depend on local events [48]. K_{IC} has been shown to adjust with crack size because of differences in energy consumption and crack branching at the crack tip [48]. K_{IC} bending or flexural standards most often include large artificial flaws much larger than the normal statistical population of sample defects that poorly reflect natural failure conditions necessary for strength-related tests [48]. The artificial flaws, orders of magnitude larger than the expected Gaussian distribution, often continue into the neutral plane region separating tensile and compressive stress areas [5, 6]. When considering K_{IC} during flexural testing and artificial flaws extending mid-depth into a fiber-reinforced composite sample, the neutral plane has been shown to be a possible limiting barrier regarding crack propagation and fracture limits [10, 11]. Span to depth ratios commonly suggested at four for many K_{IC} tests, according to ASTM Standards [49], introduce enormous shear stress error [45–47]. As a result, correction factors for K_{IC} can range from over 200 to 300% [49].

A real value for K_{IC} appears to be the ability to stress thin material sections that should reflect fracture toughness properties related to crack propagation. Concentrated stress into weaker sections should also result in relatively low standard deviations as a strength-type test. The numerous different test configurations available should help with detailed crack propagation studies where K_{IC} does not require deflection data. However, when substantially reducing material variability by testing thinner sections, a much smaller sample population of real flaws is being examined. K_{IC} short span testing might therefore be better considered for comprehensive application-specific comparative use rather than material bulk-design purposes. Regardless, material differences can be characterized appropriately by statistical test analysis, independent of the specific experimental methods. The traditional Griffith failure criterion for spontaneous crack instability at a critical load related to brittle fracture derived for K_{IC} testing [5, 6, 16–18, 48] may not necessarily be met with fiber-reinforced composites that adsorb energy locally at fracture initiation sites and force crack deflections laterally [1, 6, 10–13]. Fiber-reinforced composites during research and product development may then need broad guidelines for testing fracture toughness. General procedures for fracture toughness testing fiber-reinforced composites may be especially important when comparing ductile micromechanical V_f relationships with other materials that fail by brittle elastic fracture. Crack instability at critical load reflects the strain– energy release during force reductions, but does not necessarily represent energy methods for

strain– energy adsorbed under the elastic portion of the load– deflection curve nor the total WOF, which are the historical representations for fracture toughness. Subsequently, there does not appear to be a reliable or convenient current test method to routinely measure bulk material toughness-related properties, although WOF has traditionally been accepted [10–12, 15, 47, 50]. Therefore, to broaden the overall scope for fracture toughness testing and provide bulk material properties, standardized energy methods by strain– energy were employed and simplified using numerical integration.

The research and development hypothesis was that increased additions of 3.0 mm quartz fibers would correlate with increased fracture toughness properties in SI units of kJ/m^2 testing resilience, WOF, and SER_C , in addition to improvements in several other mechanical relationships ($\alpha = 0.05$). Also, regarding toughening mechanisms, the addition of quartz fibers would correlate with reduced crack depths ($\alpha = 0.05$) when assessed on specimens tested to 5% deflection past peak load. Differences between groups were analyzed by T-test, with unequal variances ($\alpha = 0.05$).

EXPERIMENTAL

Materials

Quartz 3.0-mm length, 9 μm diameter fibers (Saint Gobain, QPC Products, Lexington, KY) silanated with 3-methacryloxypropyltrimethoxysilane (MPTMS) (DOW Chemical, Midland, MI) were impregnated with a visible-light photocure resin at 70 wt% fibers. The resin consisted of the typical vinyl ester resin, 2,2-bis [*p*-(2'-hydroxy-3'-methacryloxypropoxyphenyl)] propane (BisGMA) (Esstech, Essington, PA) with 2.5 wt% triethyleneglycol dimethacrylate (TEGDMA) monomer (Esstech) to reduce viscosity and to improve crosslinking. Resin systems were optimized for visible-light photocuring by incorporating photo-oxidants camphorquinone (Aldrich, Milwaukee, WI; 0.6 wt%) and Irgacure 819 (Ciba, Tarrytown, NY; 1.0 wt%); and photo-reductant 2-dimethylaminoethyl methacrylate (Aldrich) 1.0 wt%. Adhesion promoter SR9016 diacrylate (Sartomer, WestChester, PA) and MPTMS organosilane were also added into the photocure resin as well, at 2.0 and 1.0 wt%, respectively.

The resultant quartz fiber-reinforced compound was then thickened with 0.3 wt% zirconia silicate filler (3M Corporation, St. Paul, MN). The zirconia silicate particulate had been milled into spheres by a proprietary process, to provide a uniform particle distribution from 10 nm to 3.5 μm . The multimodal packing utilized in this system thus reduces interparticulate distances [51], to maximize secondary bonding van der Waals forces of attraction [52], with a hydrolytically stable thickener that also has high atomic numbers to adsorb X-rays for radiographic purposes.

BisGMA and TEGDMA were then combined at a 50:50 ratio in an identical photocure resin system for the addition of 84.5 wt% or 66 vol% 3M Corp. zirconia silicate particulate, similar to the commercial Z100 ® photocure composite. The resultant paste was then used to incorporate the photocure resin preimpregnated quartz fibers from 0.0 wt% to 70.0 wt%.

A commercial photocure fiber-reinforced composite was also available as a comparison control, Alert®, (Jeneric Pentron, CT). Fibers were reported by the manufacturer to have ~40- μm lengths with 10- μm diameters. Alert fiber aspect ratios are subsequently much lower than previous estimates for a vinyl ester polymer matrix and silica-based fiber critical aspect ratio, estimated between 46 and 65 [10, 11, 34–36]. The manufacturer further indicated that fibers were added at ~1:2 ratio with glass particulate, containing high atomic number elements for a total fiber/filler concentration of 82 wt%.

Fiber Volume Percent

In micromechanics, the geometry arrangement between fibers and polymers can be described by the rule of mixtures. Accordingly, the dominant factor for V_f can be related directly to mechanical properties as a function of composite modulus or strength parameters in relation to the fiber and polymer characteristics, which should further reflect fracture toughness. Density values from the manufacturers were used to calculate volume percentages for the constituent phases, according to weight proportions (Table 1).

Fully Articulated Flexural Test Specimen Preparation

Fiber-reinforced and particulate-filled composite samples ($2 \times 2 \times 50 \text{ mm}^3$) accommodating American National Standards Institute /American Dental Association specification No.27, but for a longer test span, increased from 20 to 40 mm were prepared with a split mold clamped between two glass plates. An Epilar 3000 (3M Corporation, St. Paul, MN) system was used for the visible-light photocure initiation and monitored with a Demetron Radiometer daily, to ensure intensities of concentrated light at a wavelength of 470 nm were above 500 mW/cm^2 . The Epilar had a 12-mm diameter light guide for general photocuring. Samples were irradiated using an overlapping sequence of exposure for a total of 20 sec on the top and bottom through the glass plates, 20 sec on the top and bottom after removing the glass plates and from the sides for 1 min, each with a focused 2-mm diameter beam. Excess material was removed from each sample followed by a sanding process using silicon carbide papers down to 600 grit. Samples were then placed in a 37°C water bath for 24 hr, primarily as a control for a uniform postcure before mechanical testing.

Mechanical Testing

Fully articulated four-point bend fixtures had been assembled by MTS Corporation for advanced ceramics, with a 40-mm span length using ¼-point 20-mm spaced loading noses. A MTS machine (858 MiniBionix) with a crosshead speed of 0.5 mm/min was conventionally used to mechanically test flexural properties. Sample size estimates were performed, so that four specimens from each group were tested.

The 50:50 BisGMA:TEGDMA photocure resin used in the initial zirconia silicate particulate-filled composite was also prepared for mechanical testing. To accommodate increased strain associated with an unfilled polymer resin, a fixture having a deeper well between the 40-mm test span was fabricated.

Fracture Toughness analysis using mechanics-of-materials energy methods for strain energy (kJ/m^2): Historically, energy under the load–deflection curve has been used to measure

sample cross-sectional area toughness as a bulk material property. With the support of computer spreadsheet technology, toughness energy values can be calculated by summing successive complementary load– deflection data points using numerical integration by the trapezoidal rule [10, 14], where from Eq. 5

$$\text{Area} = \sum \frac{1}{2} (\text{force}_1 + \text{force}_2) (\text{deflection distance}) \quad (6)$$

Data entry was simplified with Microsoft Excel, whereby constructed formulas were applied from load– deflection data couples and entered in an adjacent cell column. The cell with trapezoidal formula was subsequently copied down the same column for the corresponding load– deflection data series of repeating trapezoidal formulas. Typical newton-millimeter load– deflection data when summed as energy in millijoules and divided by the sample cross-sectional area in square millimeters converted directly to standard international units as kJ/m². Additional costly electronic integrators, software, or time consuming graph paper calibrating, cutting, and weighing necessary for measuring area under the load– deflection curve [15] were therefore eliminated with a convenient, accurate method directly related to conventional mechanical testing [10]. With fully articulated self-adjusting fixtures, deflections may reverse so that a negative trapezoidal area is balanced by a correspondingly larger positive area. As the deflection between data sets tends toward zero and number of data points increases, the error approaches zero [14]. Characteristic MTS curves, with deflection recordings averaging ~0.002 mm, each across 1,000 –3,000 data point sets, will produce accuracy to approximately five places by numerical integration, using the trapezoidal rule [14].

Resilience—Energy was integrated by numerical methods from the load– deflection curve in the elastic region up to yield point. The yield point was set at the position where the initial steep straight-line slope deviates toward increased deflection. Energy was converted to toughness as the sample cross-sectional area [10].

Work of Fracture—The area under the load– deflection curve out to a maximum of 5% deflection past the peak load was integrated by numerical methods to obtain WOF energy and converted to toughness as the specimen cross-sectional area [10].

Strain Energy Release—In order to account for crack propagation in fiber-reinforced composites, the area under the load deflection curve from peak load to maximum 5% deflection past the peak force was integrated by numerical methods as a function of the material cross-sectional area for values (Fig. 1) of the SER_{IC} [10]. The process utilized data from the load versus deformation relationship, with deformation taken from the testing machine fixture displacement rather than the specimen per se. Energy was integrated by numerical methods for area during Mode I (I) Euler tensile flexural bending under the load– deflection curve from peak load to a maximum of 5% deflection past the highest force. SER_{IC} toughness is then a function of energy relative to the material cross-sectional area. With small SER_{IC} deflections less than 1% of the total for example when no fibers are added, judgment might be considered to look for deflection points that become lower

because of rapid release of the platen load on the sample, such that a single load–deflection data set negatively impacting the total area could be discarded, as indicated by analysis before summing all trapezoidal areas. When testing low strength materials, fracture noise could be eliminated using an appropriate scaled-down load cell for better data resolution.

In order to compare fracture toughness with other mechanical properties, flexural strength, and modulus were calculated according to the following equations:

$$\text{Flexural strength } (S_F): S_F = 3FL/4bd^2 \text{ ASTM D6272 – 00} \quad (7)$$

$$\text{Flexural modulus } (E_F): E_F = 0.17L^3M/bd^3 \text{ ASTM D6272 – 00} \quad (8)$$

Specifying F = maximum load, L = span length, b = sample width, d = sample depth, M = slope of the tangent to the initial straight line on steepest part of the load–deflection curve.

Percent load-retained capacities were calculated by dividing the strength at 5% deflection past peak load by the maximum flexural strength. Related to this quantity, fibers not only bridge cracks to prevent complete failure but also tend to accumulate damage away from the primary crack, so that testing normally does not result in complete failure at 5% deflection past maximum load, even at low fiber fractions [10–12]. The upper fixture attached to the MTS mechanical test machine was visually monitored from the digital output. An estimate of any potential retained load could be approximated at 5% deflection past the maximum flexural bending force, where testing was then stopped so that fractures initiating from the flexural tensile surface could be evaluated. Mechanical variables could then be assessed as theoretical predictors for fracture crack propagation.

Fracture Analysis

MicroVu metrology with a calibrated accuracy to 0.1 μm along the x and y -axes was used to measure the primary surface fractures that extended from the flexural tensile surface. Reflected light microscopy (Nikon Microscope) provided general fracture image comparison for fracture depth measurements (10 $\times$ to 30 $\times$ magnification). The vertical fracture depths measured from the tensile failure side were normalized as a function of the sample thickness for evaluation of the various mechanical properties. Normalized crack-depth measurements were taken from both lateral sides and averaged [10].

Characterization

Scanning Electron Microscope—Composite specimens were prepared after MicroVu and Nikon imaging for crack analysis (SEM Philips). Scanning electron microscope (SEM) provides a large depth of field that is ideal for imaging deep fractures, in addition to high resolution for surface details. Samples from each group were viewed from the lateral surface to show the extent of material fracture, depth-wise from the tensile flexural surface, and characterize the presence of typical damage for each V_f group. Before SEM imaging, samples were gold/palladium sputter-coated.

Samples surrounding the average median moduli for each V_f group were also chosen for imaging, to characterize fiber orientation related to ROM micromechanical analysis. The resulting samples were first sectioned distal and away from the primary fractures. Distal-cut sample sections were then prepared by first inserting diamond blade saw cuts parallel to the top and bottom surfaces at each end, in order to cleave material parallel to the general fiber direction along the long axis of the sample [10].

RESULTS AND DISCUSSION

Flexural Mechanical Testing

Incorporating 3.0 mm quartz fibers into a zirconia silicate particulate-filled photocure composite showed strong improvements in all mechanical properties tested. Following increasing improvements in the properties evaluated with the addition of fibers, a plateau region was commonly reached at 28.2 V_f , where regression linearity then changed. Separate failure processes that produced a deviation in linearity in the range of 28.2 V_f are depicted in the charts (Figs. 2–4) with dashed (0.0–28.2 V_f) and dotted lines (28.2–54.0 V_f). Interpretations from micromechanics could be used to explain variability around the regression lines for fracture toughness and other mechanical properties versus V_f properties through the analysis for coefficient of determination (R^2).

When evaluating a regression equation, the R^2 compares the scatter of X and Y data pairs to the mean for Y (total deviation) and the regression line distance to the mean for Y (explained deviation). R^2 measures how well a line fits for data points between the independent X values for the sample regression equation to the observed dependent values of Y by a theoretical relationship using the linear equation. In this case, X is represented by V_f and Y by the mechanical property under consideration. R^2 then provides the magnitude of the explained sum of squares by the ratio of the total sum of squares, which in turn gives an indication of the amount of variation or percent explained by the regression [53].

Fracture Toughness—Incorporating 3.0 mm quartz fibers into a zirconia silicate particulate-filled photocure composite showed improvements in all fracture toughness properties tested. Adding quartz fibers to the particulate-filled composite increased resilience from ~3.0 kJ/m² to over 23 kJ/m² (Fig. 2). Adding quartz fibers to the same photocure particulate-filled composite increased WOF from about 4.5 kJ/m² to ~30 kJ/m², Fig. 3. Incorporating quartz fibers to zirconia silicate particulate-filled photocure composite increased SER_{IC} from ~0.04 to 2.4 kJ/m², a 60-fold increase (Fig. 4). When evaluating such large SER_{IC} increases, resistance to crack initiation and propagation by adding fibers to a particulate-filled composite should be considered in relation to sudden complete brittle failure. Significant fracture toughness differences between the zirconia silicate particulate-filled composite and fiber-reinforced composites began when adding fiber reinforcement at 10.3 V_f for resilience, 5.4 V_f for WOF and 5.4 V_f for SER_{IC} ($p < 0.05$).

Variability around the regression lines for fracture toughness could be explained by V_f for the properties as resilience, WOF, and SER_{IC} measured through R^2 values at 61, 66, and 61%, respectively (Figs. 2–4). The majority of significant differences for progressive fracture toughness increases with fiber addition occurred before 28.2 V_f . Separate

mechanical processes were apparent as the fiber fractions increased above 28.2 V_f . Observe that between 28.2 and 54.0 V_f , correlation coefficients for fracture toughness properties all became negative. Before 28.2 V_f , fibers dominated the properties and showed increasing values for both resilience and WOF, with R^2 values of 0.82 and 0.91, respectively. Above 28.2 V_f , the same R^2 values for resilience and WOF declined dramatically to 0.10 and 0.01, respectively, as negative correlation coefficients. A correlation for SER_{IC} between 0.0 and 28.2 V_f provided a R^2 of 0.68, whereas the correlation between 28.2 and 54.0 V_f R^2 drops to just 0.03, with a negative correlation coefficient. Increasing fiber volume fractions have generally been shown to increase fracture toughness [13, 54–56]. However, reduced resin impregnation of the fibers creating atomic scale Griffith-type cracks at the critical polymer/fiber interface was thought to prevent further fracture toughness improvements above 28.2 V_f . Mechanical property deviations from linearity have been previously observed in fiber-reinforced composites because of flaws related to porosity and fiber misalignment at higher fiber volume fractions [1, 57, 58].

When compared to the neat photocure resin–polymer system, both the zirconia silicate particulate-filled composite and silica-based filler with silica microfibers in commercial Alert produced considerably lower fracture toughness values measuring resilience, WOF and SER_{IC} (Figs. 2–4). Resilience fell from ~9.2 kJ/m² for the photocure resin polymer to 3.2 kJ/m², with 0.0 V_f zirconia silica particulate and 1.5 kJ/m² with commercial Alert. The polymer WOF declined from 16.2 to 4.5 kJ/m² for 0.0 V_f zirconia silicate and 3.2 kJ/m² for Alert. SER_{IC} fracture toughness dropped from a mean group neat resin polymer value of 0.25 kJ/m² down to 0.04 kJ/m² and 0.03 kJ/m² for filled composites with 0.0 V_f zirconia silicate particulate and Alert with microfibers, respectively. Differences for resilience, WOF, and SER_{IC} between the photocure polymer and both zirconia silicate particulate-filled composite or Alert with microfibers were significantly different ($p < 0.05$). Related to fiber-reinforced composites, large polymer strains have been considered an important toughening mechanism to reduce shearing at the fiber ends [10].

Mechanical Property Comparisons for Flexural Strength and Modulus—Adding 3.0 mm quartz fibers to the zirconia silicate particulate-filled composite showed a ~3.5× increase in strength from 118 MPa to over 400 MPa (Fig. 5). The V_f could explain 85% of the variability for flexural strength calculated through R^2 (0.8527). Adding quartz fibers to the zirconia silicate particulate-filled composite produced good linearity for modulus across the range of fiber fractions from 0.0 to 54.0 V_f (Fig. 6). The modulus for fiber-reinforced composites increased over twice the value for particulate-filled composites. V_f could explain 93% of the variability for modulus calculated through R^2 (0.9265). Addition of 66 vol% (84.5 wt%) zirconia silicate particulate filler to the photocured neat resin polymer significantly increased the modulus ($p < 0.05$). When comparing the polymer to Alert with 82 wt% filler containing ~26 vol% microfibers, the modulus again significantly increased ($p < 0.05$).

Percent Load Retained at 5% Deflection Past Maximum Force—During crack propagation, fibers not only participate in crack resistance through providing high strengths, but also deflect cracks to dissipate energy by polymer debonding, in addition to frictional

fiber pull with fiber bridging. At higher fiber concentrations, samples still retained a large majority of the maximum load at 5% deflection past the peak force (Fig. 7). A plateau for % load retained appeared to develop again near 28.2 V_f . Fibers also participated to prevent full brittle fracture failure even at low volume percentages.

Crack Propagation Depths—Fracture depths were normalized by the sample thickness depth for analyses with the mechanical properties (Fig. 8). The influence of V_f could be used to explain 86% of the variability for the decrease in crack depth results. Before 28.2 V_f , fibers dominated the properties, experiencing decreasing values for crack depth with a R^2 value of 0.891. Above 28.2 V_f , the R^2 value for crack depth fell to 0.1991. Again, little change was noted above 28.2 V_f , possibility due to poor wetting of the fibers by the resin. Voids and fiber misalignment have been identified, with loss of linear strength increases at higher volume fractions due to voids and fiber misalignment [1, 57, 58]. Also, at higher fiber fractions, fiber/fiber interactions would tend to cause shear against the weaker polymer matrix during tensile stress.

Scanning Electron Microscopy

Lateral views of representative samples were used to characterize the extent of fracture penetration, as fiber fractions increased (Figs. 9A–9F). Without fibers at 0.0 V_f , fractures penetrated cleanly through all samples tested with minimal SER_{IC} . As fiber fractions increased, crack depths decreased. With 5.4 V_f , no sample fractured through completely at ~5% deflection past peak load. Below 28.2 V_f , deep fracture penetration reached well above the neutral plane and presented open fractures with 45° oriented crack space openings at 10.3 and 19.8 V_f (Figs. 9A and 9B). Fiber bridging mechanisms appeared to occur at 19.8 V_f (Fig. 9B). By 28.2 V_f , the 45° oriented cracks were closed with primary fractures, exhibiting transverse splinters on the tensile surface (Fig. 9C). Previous work has shown that mechanical properties are considerably higher when cracks do not extend past the neutral plane [10], which was demonstrated in this investigation primarily by virtue of increased V_f . At 54.0 V_f , the 45° oriented cracks were minimal, with transverse cracks propagating in thin sections on the tensile surface as the common mode (Fig. 9F). Experimental observations have formerly shown crack restriction at low fiber fractions, while at higher V_f s cracks deflect closer to the composite surface related to polymer/fiber debonding [6, 13]. In addition to fiber breakage, cracks were deflected laterally, with debonding energy required to separate the matrix polymer and fibers, while fiber pull-out appeared to occur as another energy-adsorbing mechanism during crack propagation.

Samples viewed following specimen preparation by a cleavage process showed well-aligned fibers parallel to the long axes of the specimens. During SEM characterization, some fiber lengths for the Alert were noted to be longer, than reported by the manufacturer of 40 μm , which has been previously observed [59].

Mechanical Variables as Fracture Predictors

The correlation coefficient (R) is another measure of the influence for a linear relationship [53], for example between V_f and a mechanical test variable. R then is the positive or negative square root of the coefficient of determination (R^2) previously used for analysis.

The magnitude of R can also be used to provide a test statistic based on a T-test related to R , R^2 and the sample size to determine a p value, regarding the probability of error when claiming the validity of a research hypothesis [53]. The governing fiber contribution to composites measure by V_f correlated significantly with all mechanical test variables ($p < 0.0000005$, Table 2). Each variable tested for the fiber-reinforced molding compound provided consistent results related to fracture crack propagation, all negatively correlating to reduce crack depth and having probabilities for making an error in this assertion at $p < 0.0000005$. Correlation coefficients for fracture depth with fracture toughness variables measured resilience ($R = -0.785$), WOF ($R = -0.814$), and SER_{IC} ($R = -0.798$). V_f ($R = -0.938$), modulus ($R = -0.910$ as a negative value and not positive), and flexural strength ($R = -0.898$) stood out as strong predictors for material fracture with regard to open crack depth. All variables correlated with one another significantly ($p < 0.000001$).

When examining the correlation matrix analysis, the highly significant uncertainty values for $p < 0.000001$ should be recognized. The overriding fiber involvement in composite material properties cannot be overestimated. In addition, information provided at such significance might be used for a single variable to estimate other mechanical parameter influences for future investigations, where sample sizes or V_f groups may not be as large. Single predictors are then further available to take advantage of increasing digital equipment technology, with high sensitivity for measuring individual mechanical variables toward more complete material analysis, especially for materials dominated by fiber reinforcement. Energy adsorption measured through fracture toughness variables should be considered with regard to safety factors in the material elastic stress region and also over long-term cyclic fatigue where permanent deformation may occur. SER_{IC} uniquely provided information regarding the type of crack propagation, comparing brittle full fracture with little measured energy released to ductile high energy consumption with only partial failure.

Fully-Articulated Four-Point Euler-Type Flexural Testing

A progressive design with high-tech materials was performed toward ideal flexural bend testing by minimizing top-load shear effects. Advanced ceramics ASTM/MilSpec standards were combined with polymer ASTM standards, to include fully articulated fixtures with a 40-mm span and 2-mm sample depths, to reduce large shear effects. Fully articulated fixtures reserved to compensate for lack of sample parallelism were employed according to the ASTM standard on advanced ceramics C-1161-94 [43]. Also, fourpoint loading was preferred over three-point to stress more of the material [43, 44]. High silica content quartz fibers were utilized to optimize vinyl ester polymer coupling with a methacrylate vinyl functional organosilane [28, 29]. Photocuring was then used to minimize thermal cure stresses [1, 40]. Subsequently, the model test performance demonstrated correlations with highly significant p values for the mechanical properties evaluated.

By comparison with the 40-mm flexural span testing composites and same 3.0-mm, 9.0- μ m diameter quartz fibers, similar independent test data validation by the United States Department of Energy, using a shorter 20-mm fully articulated four-point span and the same 2.0-mm sample depth [11, 12], is provided in Table 3. A test span to sample depth ratio (S:D ratio) less than 16 is considered too low to prevent load shear according to ASTM standard

D 6272–00 [45]. Increased shearing effects for the 10 S:D ratio 20-mm span when comparing the 20 S:D ratio 40-mm span should therefore reduce mechanical properties, which were found for WOF, modulus, and flexural strength. Other researchers have previously indicated that S:D ratios greater than 20 are necessary when testing fiber-reinforced composites [46, 47].

SUMMARY

Addition of 3.0-mm quartz fibers to zirconia silicate particulate-filled composite increased mechanical properties and particularly fracture toughness values, while reducing sample crack penetration depths. Numerical integration using the polygon quadrilateral trapezoid was employed for fracture mechanical analysis by energy methods for strain energy from the load– deflection curve. Fracture toughness properties significantly increased with V_f ($p < 0.0000005$), and all variables correlated with one another significantly with $p < 0.000001$. Fracture toughness values were influenced convincingly by fiber reinforcement measuring resilience, WOF, and SER_{IC} , which showed increases above the particulate-filled composite to levels of $\sim 7\times$, $6\times$, and $60\times$, respectively. By adding fibers to a particulate-filled composite, modulus doubled and strength increased to about $3.5\times$ for the two best mechanical property correlation matrix fracture predictors. Significant fracture toughness differences between the zirconia silicate particulate-filled composite and fiber-reinforced composites began when adding fiber reinforcement at $10.3 V_f$ for resilience, $5.4 V_f$ for WOF, and $5.4 V_f$ for SER_{IC} . SEM fracture surfaces were consistent with interpretations of the mechanical test data and fracture depth measurements. Flexural test spans 40.0-mm long, with 2-mm deep samples, in this study, extensively improved mechanical properties and fracture toughness over identical independent testing by the United States Department of Energy using 20.0 mm flexural spans, which must be considered when testing for absolute mechanical properties.

CONCLUSIONS

Test results validate the research and development hypotheses that photocured particulate-filled composites can be reinforced with quartz fibers for significant improvements in fracture toughness and related mechanical properties. Fiber-reinforced technology with improved mechanical properties that include material toughening should therefore extend service projected for use in medical/dental devices or other components, to prevent fracture or chipping commonly seen near thin sections. The neutral plane appeared to be a limiting barrier to crack propagation, with a sufficient concentration of fibers, so that cracks penetrating below demonstrated greatly improved mechanical properties compared to cracks extending above midplane. Further contributions are expected by supplying a convenient load– deflection energy measurement using numerical integration, with the Microsoft Excel Sum function to encourage global publication of toughness bulk material properties for future analysis. When considering the ease by which toughness measurements can be numerically integrated, past load– deflection data results could even be re-examined and compared with conventional mechanical properties previously published. By including energy-method strain– energy data as WOF, the entire load– deflection curve is better defined with maximum strength and modulus, so that commonality can be achieved for

research intercooperation. Including resilience and SER_{IC} then defines the entire load–deflection curve of greatest interest.

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Abbreviations

C	Critical load or stress where fracture occurs. In mode I tension critical stress C is reached such that fracture occurs when $C = IC$ [48]
G	Strain energy release rate (kJ/m^2)
I	Mode I tension
SER	Strain energy release (kJ/m^2)
WOF	Work of fracture (kJ/m^2)

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FIG. 1.

Typical load– deflection curves for particulate-filled composite at 0.0 V_f and 3.0 mm quartz fiber composite at 28.2 V_f , depicting strain energy release areas after critical loading of maximum force. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 2.

Group mean resilience for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0 –54.0 V_f broken down into separate correlations 0.0 –28.2 V_f and 28.2–54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 3.

Group mean WOF for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0 –54.0 V_f broken down into separate correlations 0.0 –28.2 V_f and 28.2–54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 4.

Group mean SER_{IC} for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0 –54.0 V_f broken down into separate correlations 0.0 –28.2 V_f and 28.2–54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 5.

Group mean flexural strength for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0–54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 6.

Group mean modulus for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0 –54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 7.

Group mean %postload (5% deflection past maximum force) for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 8.

Group mean degree of crack propagation for zirconia silicate particulate-filled composite with addition of 3.0 mm quartz fibers. Correlation regression line 0.0–54.0 V_f broken down into separate correlations 0.0–28.2 V_f and 28.2–54.0 V_f . Photocure resin polymer and commercial photocure Alert composite for comparisons. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 9.

(A) Brittle vertical crack with 45° shearing fiber pull-out evident. ($10.3 V_f$, $\times 30$ magnification, Scale bar = 500 μm); (B) Brittle vertical crack with 45° shearing fiber pull-out evident, with possible crack bridging. ($19.8 V_f$, $\times 30$ magnification, Scale bar = 500 μm); (C) Transverse surface splinter with unopened 45° shear crack. ($28.2 V_f$, $\times 30$ magnification, Scale = bar 500 μm); (D) Transverse cracks deflected with diffuse damage. ($35.8 V_f$, $\times 30$ magnification, Scale bar = 500 μm); (E) Transverse cracking above the lower tensile surface. ($42.8 V_f$, $\times 30$ magnification, Scale bar = 500 μm); (F) Transverse surface crack deflection

with numerous areas of fiber breakage on the lower surface. ($54.0 V_f$, $\times 30$ magnification, Scale bar = 500 μm).

TABLE 1

Compound formulations volume percentages.

Wt% fibers	Quartz fibers (V_f)	Zirconia silicate (vol%)	Bis-GMA (vol%)	TEGDMA (vol%)
0 wt% sample group 1	0.0	66.0	18.1	15.9
5 wt% sample group 2	5.4	61.8	18.1	14.7
10 wt% sample group 3	10.3	56.5	20.2	13.0
20 wt% sample group 4	19.8	42.8	26.1	11.3
30 wt% sample group 5	28.2	32.7	30.3	8.8
40 wt% sample group 6	35.8	23.5	34.1	6.6
50 wt% sample group 7	42.8	15.1	37.6	4.5
70 wt% sample group 8	54.0	1.6	43.2	1.2

The Alert® fiber volume fraction is estimated at ~26 vol%. 2.2, 3.1005, 1.14, 1.07 are the densities (in gram per cubic centimeters) of quartz fiber, zirconia silicate, bis-GMA, and TEGDMA.

TABLE 2

Pearson product correlation coefficient (*R*) matrix (*p*-values).

Variable	Fiber volume percent	Resilience	Work of fracture	Strain energy release	modulus	Flexural strength	Degree vertical fracture
Volume percent	1.000000 (0.000000)	0.779196 (0.000000)	0.814814 (10 ⁻⁷)	0.779323 (0.000000)	0.962555 (10 ⁻¹⁷)	0.923391 (10 ⁻¹³)	-0.938266 (10 ⁻¹³)
Resilience	0.779196 (0.000000)	1.000000	0.931357 (10 ⁻¹³)	0.798731 (10 ⁻⁷)	0.753125 (0.000001)	0.912809 (10 ⁻¹²)	-0.784891 (0.000000)
Work of fracture	0.814814 (10 ⁻⁷)	0.931357 (10 ⁻¹³)	1.000000	0.868571 (10 ⁻⁹)	0.797212 (10 ⁻⁷)	0.951549 (10 ⁻¹⁶)	-0.813671 (10 ⁻⁷)
Energy release	0.779323 (0.000000)	0.798731 (10 ⁻⁷)	0.868571 (10 ⁻⁹)	1.000000	0.780418 (0.000005)	0.830789 (10 ⁻⁸)	-0.797759 (0.000000)
Modulus	0.962555 (10 ⁻¹⁷)	0.753125 (0.000001)	0.797212 (10 ⁻⁷)	0.780418 (0.000000)	1.000000	0.905629 (10 ⁻¹¹)	-0.910127 (10 ⁻¹¹)
Flexural strength	0.923391 (10 ⁻¹³)	0.912809 (10 ⁻¹²)	0.951549 (10 ⁻¹⁶)	0.830789 (10 ⁻⁸)	0.905629 (10 ⁻¹¹)	1.000000	-0.897955 (10 ⁻¹⁰)
Vertical crack	-0.938266 (10 ⁻¹³)	-0.784891 (0.000000)	-0.813671 (10 ⁻⁷)	-0.797759 (0.000000)	-0.910127 (10 ⁻¹¹)	-0.897955 (10 ⁻¹⁰)	1.000000

TABLE 3

Fully articulated four-point flexural 20-mm and 40-mm test span lengths.

20 mm span (S:D ratio 10)			40 mm span (S:D ratio 20)		
WOF 5% δ past peak load (kJ/m ²)	Flexural strength (MPa)	Modulus GPa	WOF 5% δ past peak load (kJ/m ²)	Flexural strength (MPa)	Modulus (GPa)
84.5 wt% zirconia silicate commercial			84.5 wt% zirconia silicate prepared fresh		
1.08	64.4	13.7	4.48	117.6	19.5
35 wt% 3.0 mm quartz fibers added			30 wt% 3.0 mm quartz fibers added		
11.28	227.2	19.8	30.1	374.9	31.5

p < .001 for all comparisons between 20-mm and 40-mm test spans (*t*-test unequal variances). δ , deflection.