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Micromechanics for Fiber Volume Percent With a Photocure Vinyl Ester Composite

Richard C. Petersen¹, Jack E. Lemons^{1,2,3}, and Michael S. McCracken^{1,3}

¹Department of Biomedical Engineering, School of Engineering, University of Alabama at Birmingham, Birmingham, Alabama

²Department of Surgery, School of Medicine, University of Alabama at Birmingham, Birmingham, Alabama

³Division of Biomaterials, School of Dentistry, University of Alabama at Birmingham, Birmingham, Alabama

Abstract

Micromechanics for fiber volume percent (V_f) from 0.0 V_f to 54.0 V_f were conducted using (3 mm long $\times$ 9 μ m diameter) high-purity quartz fibers in a visible-light vinyl ester particulate-filled photocure resin. MTS fully articulated four-point bend fixtures were used with a 40 mm test span and 50 $\times$ 2 $\times$ 2 mm³ sample dimensions. Specimens were tested following the combined modified ASTM standards for advanced ceramics ASTM-C-1161–94 and polymers ASTM-D-6272–00 for modulus, flexural strength, and yield strength. Experimental data provided reliable statistical support for the dominant fiber contribution expressed through the rule-of-mixtures theory as a valid representation of micromechanical physics. The rule-of-mixtures micromechanics described by V_f could explain 92, 85, and 78% of the variability related to modulus, flexural strength, and yield strength respectively. Statistically significant improvements with fiber addition began at 10.3 V_f for modulus, 5.4 V_f for flexural strength, and 10.3 V_f for yield strength, $p < 0.05$. In addition, correlation matrix analysis was performed for all mechanical test data. An increase in V_f correlated significantly with increases in modulus, flexural strength, and yield strength as measured by the four-point bending test, $p < 10^{-10}$. All mechanical properties in turn correlated highly significantly with one another, $p < 10^{-9}$.

INTRODUCTION

Reinforced molding compounds are commonly manufactured with discontinuous fibers in a resin matrix containing particulate filler. Fibers provide reinforcement whereas filler particulate also assists in resin thickening and more efficient homogeneous consolidation of the composite [1–5]. In addition, particulate filler can be used to improve specific material properties, such as reduced cure shrinkage and part warpage, flame retardancy, thermal or electrical conductivity, reduced weight, higher density (radio-opacity), greater hardness, or lower surface friction as examples [2–5]. Discontinuous fiber-reinforced composites

facilitate the molding of complex curved spaces and typically use fibers well above the critical length (L_c) or critical aspect ratio (L_c/d) to ensure stress transfer between the fibers and matrix [1]. Related to the polymer/fiber interfacial shear bond strength interface, the silica-based fiber polymer matrix composites have experienced widespread success in part due to possibilities for organosilane coupling to form chemical/reversible links with the resin matrix [1, 6]. With regard to successful polymer/fiber shear bond strengths, vinyl esters with unsaturated polyester composites are a major class of polymer materials that enjoy a worldwide market with approximately 4.4 billion pounds produced annually [7]. Because of 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 [8–11]. Stress transfer has been theoretically modeled whereby fiber strengths are not expected to contribute to a composite before $2L_c$ [12, 13]. In addition, mechanical properties have been shown to plateau for fiber lengths at about $4-5L_c$ [13–15]. Therefore, to investigate the micromechanics for basic properties, 3.0 mm length, 9.0 μm diameter, high purity (99.99% silica) quartz fibers, at approximately $6L_c$, were considered for incorporation into a photocure vinyl ester molding compound. The pure quartz fibers were also expected to maximize silane polymer bonding between the matrix and reinforcement/fillers for enhancing properties and related testing. The organosilane-coupled quartz fibers with virtually no lattice structure impurities can further provide hydrophobic chemical resistance and thereby almost zero water solubility [16–18].

Photocure technology provides an alternative system to thermal-type methods, whereby fibers can be processed with a monomer resin for subsequent curing using photons as the energy to initiate polymerization [19]. Accordingly, small parts can be photocured with visible-light in relative short time periods, measured in tens of seconds [20]. By comparison, curing times for ultra violet light (UV) photocure structural applications are measured in minutes and thermal curing measured in hours [21]. In addition, photon energy having a longer wavelength within the visible-light region has been shown to be more efficient than UV energy for curing deeper parts [20], as an important requirement for fiber-reinforced composite molding compounds. Accordingly, UV energy is primarily restricted for curing inks and coatings where quick photon activation and line speed is the major concern [19]. Photocuring also reduces possible detrimental thermally induced internal shrinkage stresses that could influence structural relationships during mechanical deformation and fracture crack propagation [1, 4, 19, 20]. As an example of visible-light technology, a photocure 3.0-mm discontinuous fiber-reinforced composite independently evaluated by the United States Department of Energy has demonstrated decisive improvements in mechanical properties when compared to the identical particulate-filled commercial dental compounds without fibers [8, 22]. Improvements in fiber-reinforced mechanical properties increased even more by increasing flexural test span to sample depth ($S:D$) ratios from 10 to 20 [8, 13, 22]. Such mechanical test result improvements are related to recommendations for $S:D$ ratios of at least 20, which have been suggested for fiber-reinforced composites [23, 24] and even more according to ASTM D 6272–00.

A primary objective of the present study was to provide design level information for the future research and development of fiber-reinforced molding compounds.

One goal was to develop a fiber-reinforced polymer-based dental composite to replace amalgam alloy fillings. Historically, glass fiber “wool” was initially considered by German researchers in the 1930s as a dental restorative material during the original investigations into chemically cured thermoset acrylics [25]. Dental composite material progress has been relatively slow where current particulate-filled composites suffer from relatively low strengths [26], difficulty in placement, possibility of creating voids in hard to see areas, and limitations in restoring contacts between teeth for proper operative restoration [27]. In contrast, molding compounds with 3.0-mm fibers can provide a positive pressure environment during placement to minimize voids and capacities for re-establishing interproximal contacts [28], in addition to greatly improving common mechanical properties [8, 13, 22, 28].

Photocured fiber-reinforced molding compounds are currently under research and development to restrict relative micromotion planned for bonding to epoxy/carbon fiber-reinforced cranio-maxillo-facial reconstruction devices and full-mouth reconstruction frameworks. Visible-light photocuring was also considered as a nonthermal process to replace chemical cure acrylic used for cranioplasty that is associated with “burning” the brain [29, 30]. When compared to a near zero-porosity vacuum manufacturing process for photocured composites, chemical cure introduces substantial air voids during mixing [31]. Related materials that might benefit from photocure molding compound technology include fiber-reinforced adhesives and thermally sensitive components requiring molding protection, such as tamper-resistant, more rugged, and corrosion resistant circuit boards. Mechanical strength and overall safety factors plus low temperature photocure processing of polymerbased fiber-reinforced composites may also provide a means to incorporate numerous additives toward the high specificity required for a wide range of tissue-engineered biomaterials or thermal electronic requirements. The United States Department of Defense has previously solicited rapid repair materials for field service so that reinforced photocure molding compounds should further be applied when combined by bonding with epoxy/carbon fiber composite stiffeners and photocure woven fabric. Photocure preimpregnated composites have an advantage over onsite composite fabrication whereby they can be prepared in advance with indefinite dark storage times for ideal molding consistency, tack and drape ready for cure in addition to low energy process requirements. Visible-light photocure composites even cure under water using optical guide wave attachments. Vinyl ester/epoxy polymer matrix composites can further be connected by bonding mechanisms whereby holes required for strength reducing fasteners can be reduced in number with structural adhesives [32, 33] related to the discontinuous fiber-reinforced composites.

During research and development, for instance when incorporating fibers into a matrix to make a composite, it is important to optimize the mechanical properties. Although incorporating fibers into a particulate-filled composite might be assumed to increase mechanical properties, costs also increase as fibers are added. Commercial research and development based on the manufacturing of vinyl ester photocure fiber-reinforced composite molding compounds will require determining concentration V_f -related mechanical improvements specific to representative commercial particulate-filled bondable

photocured composites. Significant advantages related to V_f can then be compared toward increasing costs when adding fibers that include accommodating utilization of existing equipment and packaging. Accordingly, micromechanics could be examined in relation to fiber and polymer matrix properties, regarding the intergeometric arrangements to better predict mechanical improvements relative to V_f . In regard to classical micromechanics, approaches normally include examination of modulus as an essential material property related to stress/strain and especially the isostrain of all phases in the elastic region [1, 34–36].

$$\varepsilon_f = \varepsilon_m = \varepsilon_{cl} = \Delta l / l \quad (1)$$

In Eq. 1, ε is the strain for the fiber (f), matrix (m), and composite along a longitudinal direction (cl) with longitudinal deformation (Δl) for the length (l) of the composite. The loaded condition of the composite in the longitudinal direction is represented by an equilibrium of forces (F) such that

$$F_{cl} = F_f + F_m \quad (2)$$

Also, within the elastic region, stress (σ) and area (A) can be expressed in Eq. 3.

$$\sigma_{cl} A_c = \sigma_f A_f + \sigma_m A_m \quad (3)$$

Then, since during elastic strain

$$\sigma = E \varepsilon \quad (4)$$

it follows that

$$\sigma_{cl} A_c = (E_f A_f + E_m A_m) \varepsilon_{cl} \text{ during isostrain} \quad (5)$$

Subsequently dividing through by A_c gives

$$\sigma_{cl} = (E_f A_f / A_c + E_m A_m / A_c) \varepsilon_{cl} \quad (6)$$

Over the same length of a homogeneous cross-section composite, A_f / A_c and A_m / A_c would then be the volume fractions V_f and V_m for the fibers and matrix, respectively, so that

$$\sigma_{cl} = (E_f V_f + E_m V_m) \varepsilon_{cl} \quad (7)$$

and

$$\sigma_{cl} / \varepsilon_{cl} = E_{cl} = E_f V_f + E_m V_m \quad (8)$$

Equation 8 expresses the rule of mixtures in terms of Young's modulus [1, 35, 36]. An equation for composite longitudinal strength [1] can further be derived from Eq. 3, with a similar cross-section argument for volume fractions as

$$\sigma_{cl} = \sigma_f V_f + \sigma_m V_m \quad (9)$$

However, isostress mechanical properties in the transverse direction are considerably different than principle longitudinal properties [1, 36]. Therefore, since discontinuous fiber-reinforced molding compounds are not perfectly anisotropic but contain elements of random planar arrangements, Eqs. 8 and 9 can further be evaluated by efficiency factors (EFs) to account for loss of ideal mechanical properties [36]. In fact, a mechanical properties evaluation by studying the micromechanics of the fiber/polymer geometry longitudinal arrangements can be considered with EFs using statistical analysis to account for all processing variables not described by the independent V_f variable to include: fiber disorientation, fiber length, fiber strength, fiber breakage, fiber interfacial bonding with the matrix, particulate filler multimodal consolidation, void content, resin-rich areas, internal cure stresses, and plastic deformation determination strain mismatches with each constituent material as commonly described examples for possible error [1–5, 36]. All variable error not included within the independent V_f variable or dependent mechanical test variables are included in the p -level of being wrong when testing the validity of the research hypothesis. Differences between the experimental results and theoretical rule of mixtures then consist of any error introduced during sample preparation, during mechanical testing, or by the theory.

The equations regarding rule of mixtures can further be modified to account for the volume fraction of the particulate filler [4] often needed for consolidation and void control [2–5] in fiber-reinforced molding compounds as part of the volume fraction such that:

$$V_c = V_f + V_p + V_m \quad (10)$$

where V_p is the particulate filler volume fraction. This relationship assumes 100% bonding and uniform cross-section distribution, with voids practically eliminated during material formulation.

Most recent work related to discontinuous fiber-reinforced polymer matrix composites generally use a matrix with vinyl ester resin, unsaturated polyester resin, or a thermoplastic [8, 13, 22, 37–50]. Mechanical properties for strength and modulus are normally much higher for fiber-reinforced thermoset vinyl ester or unsaturated polyester composites when compared with those of fiber-reinforced thermoplastic composites [8, 13, 22, 37–50]. Mechanical properties for strength and modulus with a fiber length of 2.0 mm for a photocure composite can further be favorably compared in better detail with other discontinuous fiber-reinforced thermoset composites recently described in literature, Table 1, [8, 13, 22, 37–40]. From Table 1, the mechanical properties of photocure chopped quartz fiber-reinforced vinyl ester molding compound were higher by comparison than those of the other types of thermoset discontinuous fiber-reinforced composites for both strength and modulus. Conversely, UV-cured resins have been reported with lower mechanical properties than those of chemically or thermally cured thermoset-engineered composites [21].

The outstanding results for the photocure composite may have been due to a deliberate two-step fiber-resin preimpregnation process [8, 13, 22]. A two-step resin-fiber impregnation has

been previously recommended for fiber-reinforced molding compounds toward optimizing property levels by improving fiber wetting, reducing fiber interactions, minimizing resin-rich areas, and lowering void content [51]. Even still, the photocure vinyl ester composite tested with 2.0 mm chopped fiber lengths at about $4L_c$ [13] used fibers considerably shorter than those other thermoset composites in Table 1 that used fibers up to 50 mm as either mat or chopped fiber, where continuous strengths might be indicated.

To place the exceptional photocure results into better perspective, fiber-reinforced composites with fiber lengths less than $15L_c$ have been considered discontinuous with respect to theoretical longitudinal composite properties [36]. When regarding longer silica-based fibers with a vinyl ester resin and a respective critical aspect ratio of about 50 [8–11, 13], an approximate 10 μm fiber diameter with L_c of 500 μm projects to a $15L_c$ with fiber length of only 7.5 mm. The longitudinal composite strength (σ_{cl}) at $15L_c$ should be achieved with 97% fiber strength (σ_f) contributions, according to basic stress-transfer micromechanics by the following equation [1, 13, 36]

$$\sigma_{cl} = \sigma_f V_f (1 - [L_c/2L]) + \sigma_m (1 - V_f) \quad (11)$$

A loss of σ_f stress transfer occurs relative to the rule of mixtures because of polymer/fiber shear debonding [1, 13, 36]. Nonetheless, expected higher mechanical properties were not produced by either the thermoset chemical/heat cure mat or chopped fiber composites experimentally. Then again, earlier stress-transfer micromechanics with projected estimates for the σ_f contribution at $15L_c$ should be revised downward to about 90% because of concurrent loss of fiber volume percent during polymer/fiber shear debonding according to more recent theory for micromechanics by the following equation [13].

$$\sigma_{cl} = \sigma_f V_f ([L - L_c]/L) (1 - [L_c/2L]) + \sigma_m (1 - V_f) \quad (12)$$

Derivation of the unique variable V_f from A_f/A_c was in itself a major aspect of the proof for the rule of mixtures which should be clearly identified as a separate variable from σ_f . Identification of V_f in this way better points out the need for an additional correction factor added to the rule-of-mixtures stress-transfer Eq. 11 included in Eq. 12.

Subsequently, σ_{cl} based on a volume percent correction factor now predicts that a 97% fiber strength contribution would require about $50L_c$ for continuous strength rather than $15L_c$. So, fibers with lengths greater than 25 mm would still be expected to provide approximate continuous strengths. On the other hand, the photocure composite with a 2.0 mm fiber length at about $4L_c$ would nevertheless be expected to reach a plateau for mechanical properties [13–15] that would be within a reasonable range for a continuous strength composite at about 66% σ_f , according to Eq. 12. Increasing fiber length above $4\text{--}5L_c$ then appears to generally improve fracture mechanics and by restricting crack propagation at a greater rate than improvements for σ_{cl} [13]. Since the V_f contribution in most discontinuous fiber-reinforced composites is relatively low, additive σ_m contributions then reduce the relative importance of fiber length above the $4\text{--}5L_c$ mechanical strength plateau level, where fiber interactions can even reduce mechanical properties [13].

Therefore, composite strength comparisons from Table 1 should probably be further considered with regard to fiber orientation. As such, scanning electron microscopy imaging demonstrated deliberate orientation for the 2.0-mm chopped fiber photocure vinyl ester composite [13]. Such longitudinal alignment is then consistent with the theoretical rule-of-mixtures requirement for achieving mechanical property improvements [1, 13, 36]. By comparison, the other thermoset composites in Table 1 would be expected to have fibers with more planar isotropic orientations that would reduce composite strength by a factor of around 0.375 [36, 52]. Longitudinal fiber arrangement further improves resin impregnation opposed to planar isotropic fiber cross-over that introduces voids and also matrix shearing effects along the tensile stress axis. At approximately 66% σ_f , photocure 2.0 mm fiber length composite mechanical test result comparisons with other engineered thermoset discontinuous fiber-reinforced composites with much longer fiber lengths in Table 1 were nevertheless remarkable.

Advanced ceramic specifications ASTM C 1161–94, MIL-STD-1942 (MR), and polymer standards ASTM D 6272–00 [53] are based on small samples, for a lower probability of material imperfections [1], with evaluations by flexural bend testing. In addition, four-point loading is preferred over three-point loading in order to stress a larger portion of the material [54, 55], which is particularly important during research and development. Fully articulated fixtures will further reduce errors in sample parallelism [55] and thereby should provide lower statistical deviations. Since the loading platens in four-point increase shearing when moved toward the support spans, lengthening the span is advocated to lower shearing effects [23, 24] so that shearing factors do not decrease measured mechanical values for both modulus and strengths [53, 54]. Equations from polymer standards are consequently available for four-point testing [53] as an aid for the investigation of material modulus, flexural strength, and yield strength.

The research and development hypothesis was that mechanical properties for composite modulus, flexural strength, and yield strength would increase with increasing V_f 's compared with those of particulate-filled composite controls. Statistical significance was tested at an $\alpha = 0.05$, utilizing a correlation matrix for comparative analyses.

EXPERIMENTAL

Materials

High purity quartz fibers with 3.0 mm lengths and uniform 9 μm diameters (Saint Gobain, Quartz Products Company, Lexington, KT) were used throughout these studies. In terms of quality control, the quartz fibers were 99.99% pure silica and were identified under Title III of the Defense Production Act as a strategic material to encourage availability by manufacturing development [56]. Published mechanical and physical properties for QPC quartz fibers are presented in Table 2 [16].

An advanced 3.0-mm quartz fiber discontinuous photocure resin system was previously formulated with cooperation from the United States Department of Energy, so that fibers can be combined into a vinyl ester styrene-free molding compound for significantly improved mechanical properties [8, 22]. High concentrations of the typical bisphenyl dimethacrylate

vinyl ester resin 2,2-bis [*p*-(2'-hydroxy-3'-methacryloxypropoxyphenyl)] propane (Bis-GMA) (Esstech, Essington, PA) have been used in combination with fillers and thickeners for such a moldable material. Triethylene glycol dimethacrylate (TEGDMA) monomer crosslinking agent (Esstech, Essington, PA) was added to reduce viscosity. Current strict federal regulations controlling the use of styrene [57] commonly used with most vinyl ester resins are entirely met by using the TEGDMA monomer as the alternative diluent. Quartz fibers were silanated using 3-methacryloxypropyltrimethoxysilane (MPTMS) (DOW Chemical, Midland, MI). Silane treatment of the fibers included 1.0 wt% MPTMS that was brought into solution with 70 wt% 99.5% ACS 2-propanol in distilled water and clarified by adjusting to pH 7.2 with final drying briefly at 110°C. The filler was a zirconia silicate (3M Corporation, St. Paul, MN) milled by a proprietary process for a controlled spherical particulate distribution from 10 nm to 3.5 µm diameters and silanated with MPTMS by the manufacturer. High atomic number zirconia was added to the silica for a biocompatible filler having increased X-ray radio-opacity. Bimodal and trimodal particulate systems are known to improve packing fractions over unimodal systems, where smaller particulates fill space between larger particulates [2–5]. Thus, 3M Corp. multimodal zirconia silicate facilitated compaction densities so that interparticulate distances can be minimized. Reduced interatomic distances then increase secondary bonding van der Waals forces of attraction [58], which is reflected in compound resin thickening. Enhanced packing efficiency thereby provides a means to consolidate the resultant composite and reduce voids or resin-rich areas from developing away from the reinforcing fibers [2]. Resin systems were further optimized to photocure and account for fiber reflectivity by incorporating photo-oxidants camphorquinone (CQ) (Aldrich, Milwaukee, WI), 0.6 wt% and Irgacure 819 (Ciba, Tarrytown, NY), 1.0 wt% and photo-reductant 2-dimethylaminoethyl methacrylate (Aldrich Milwaukee, WI), 1.0 wt%. Adhesion promoter SR9016 metallic diacrylate (Sartomer, West Chester, PA) and MPTMS organosilane were added into the photocure resin as well at 2.0 and 1.0 wt% respectively.

The Bis-GMA vinyl ester resin viscosity was first lowered with 2.5 wt% TEGDMA crosslinking agent. The silanated 99.99% silica quartz 3.0-mm fibers were then added to the photocure resin at 70 wt% by rotary mixing followed by alternatively applying pressure and rolling combined with a pull-combing process to align the fibers. Alignment is particularly necessary without vacuum processing and at higher fiber volume fractions for consolidation to remove porosity/voids. The extremely viscous low-diluent resin formulation was used to maximize viscosity at the fiber interface to reduce resin-rich areas from developing within the molded compound. Zirconia silicate filler was then added and mixed at 0.3 wt% to further thicken the subsequent photocure resin-preimpregnated fiber-reinforced compound.

A particulate-filled paste similar to commercial 3M Corporation dental material Z100® with 50:50 Bis-GMA:TEGDMA ratio was developed by incorporating 84.5 wt% or 66 vol% zirconia silicate silanated with MPTMS from the manufacturer. The photocure vinyl ester resin-preimpregnated fibers were then mixed in combination with the zirconia silicate particulate filler to produce composites with 0.0 –70.0 wt% fibers. Fiber, resin, and particulate were added by rotary mixing, including pressing, pulling, and rolling in repetitive

steps to form a material that could be easily placed and consolidated under pressure without producing excessive free-resin areas.

A commercial composite, Alert[®] (Jeneric Pentron, CT), was included as a comparison control for current photocure fiber-reinforced state-of-the-art technology. Fibers were reported by the manufacturer to have lengths of approximately 40 μm , with 10 μm diameters for an average aspect ratio of 4, well below the L_c/d for a vinyl ester polymer of $\sim 50 L_c/d$ [8–11, 13]. The manufacturer further indicated that fibers were added at approximately a 1:2 ratio with glass particulate with high atomic number elements for a total fiber/filler concentration of 82 wt%.

Fiber Volume Content of the Molding Compounds

Density values for quartz fibers, zirconia silicate particulate, Bis-GMA resin, and TEGDMA monomer were obtained from the manufacturers for the volume percentages shown in Table 3. Total resin volume percentages were generally higher when adding fibers, since fibers rapidly build viscosity. Conversely, as fibers are added, less hydrophilic diluent monomer was used to prevent resin-rich areas forming away from the fibers. Also as V_f 's increased, zirconia silicate V_p 's decreased. In addition, extra particulate was added at the lower V_f 's of 5.4 and 10.3 vol% because unmanageable tack developing as fibers also tend to squeeze resin toward the outer surface during packing. Filler thickening further improves molding consistency to facilitate packing during sample preparation, which has been previously described [2, 8]. Although fibers quickly dominate mechanical properties, particulate filler is essential for the fiber-reinforced molding compound process so that the paste could be consolidated to reduce void porosity and to lower resin tackiness that makes handling placement difficult (Table 4).

When considering the importance of particulate filler in the resin matrix for void control and handling during sample preparation, the total volume fractions for the composite from Eq. 10 were tested by comparing fiber additions to the particulate-filled composite such that the rule-of-mixtures formulas from Eqs. 8 and 9 could be evaluated as the following volume fractions

$$V_c = V_f + (V_p + V_m) = V_f + V_{pc} \quad (13)$$

where V_{pc} is the volume fraction of the particulate-filled composite medium, so that

$$E_{cl} = E_f V_f + E_{pc} V_{pc} \quad (14)$$

and

$$\sigma_{cl} = \sigma_f V_f + \sigma_{pc} V_{pc} \quad (15)$$

could be tested by a modified rule-of-mixtures methodology.

Fully Articulated Flexural Test Specimen Preparation

Samples $2 \times 2 \times 50 \text{ mm}^3$ accommodating an adapted American National Standards Institute (ANSI)/American Dental Association (ADA) specification no. 27 for a 40-mm test span

instead of a 20-mm span were prepared with a split mold clamped between two 12.6 mm thick glass plates. An Epilar 3000 instrument (3M Corp.) used for the photocure initiation was monitored with a Demetron radiometer daily to ensure intensities of focused visible-light at a wavelength of 470 nm and a power density above 500 mW/cm². The Epilar had a 12 mm diameter light guide for general photocuring. Samples were irradiated by an overlapping sequence for a total of 20 s on the top and bottom through the 12.6 mm thick glass plates, 20 s on the top and bottom after removing the glass plates, and from both sides for 1 min each with a focused 2 mm diameter beam. Excess material was removed from each sample followed by a sanding process finishing with 600 grit silicon carbide paper. Samples were then placed in a 37°C water bath for 24 h, primarily as a control for a uniform postcure before mechanical testing.

Mechanical Testing

Fully articulated four-point bend fixtures were obtained from MTS Corporation for advanced ceramics with a 40 mm support span length using ¼ point 20 mm spaced upper loading platens. A MTS inspection machine (858 MiniBionix) with a static cross head speed of 0.5 mm/min was used to mechanically test flexural properties. The following formulas were used to calculate:

$$\text{Flexural Strength}(F_{S_F}): F_{S_F} = 3FL/4bd^2 \text{ASTMD6272} - 00 \quad (16)$$

$$\text{Flexural Modulus}(E_F): E_F = 0.17L^3M/bd^3 \text{ASTMD6272} - 00 \quad (17)$$

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.

Yield Strength—Yield strength was calculated from the flexural strength formula by Eq. 16 where the initial steep portion of the force– deflection curves started to deviate from linearity toward increased deflection. The yield strength magnitude also placed an upper limit check on determining the slope for flexural modulus.

Polymers—A second fixture with a 40 mm length support span and having a deepened well was fabricated so that large deflections experienced with unreinforced neat resin polymers could be compared.

Deflections Past Maximum Load—The upper fixture attached to the MTS mechanical test machine was visually monitored and compared with the digital output. An estimate of any potential retained load could be approximated at 5% deflection past the maximum flexural bending force. At this magnitude, testing was then stopped so that fractures initiating from the flexural tensile surface could be evaluated at a later time.

Scanning Electron Microscopy

Samples surrounding the average median moduli for each V_f group were chosen for imaging to characterize fiber orientation. Samples were first sectioned distal and away from the primary fractures. Sample distal sections were then prepared by first making 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. Phillips scanning electron microscopy (SEM) imaging was done at 50 $\times$ and 200 $\times$ magnifications for each sample group after a gold/palladium sputter coating.

Sample Size Determinations and Statistics

Earlier results were available from quartz fiber incorporation into particulate-filled photocure composites [8, 22, 28] for a sample size determination in order to evaluate differences between groups (Table 5). Thus, four samples were used for each test group during evaluation of volume percent for addition of 3.0-mm quartz fibers into the visible-light photocure resin system. With eight groups, Table 3, and four samples each, volume percent correlations will have 32 samples. By comparison, for a sample size estimate with $\alpha = 0.01$, correlation coefficient (R) 0.85, and power of 0.95, 15 samples would be needed.

Correlation matrix analysis was applied to follow trends for mechanical properties after the addition of fibers, in addition to performing statistics for correlations among mechanical interrelationships. Statistica, Microsoft Excel with Primer of Biostatistics were employed to determine sample size, confirm data transfer, and p -values to test statistical significance set at $\alpha = 0.05$. Regression analysis was also used to develop EFs based on the rule of mixtures with experimental data compared to manufacturer fiber values. T -test by unequal variances was used to test for differences between groups, at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Mechanical Test Results and Fiber Rule-of-Mixtures Efficiency Factors

Modulus values increased relatively consistently from 19.5 GPa with the zirconia silicate particulate-filled composite group to 42.0 GPa with the 54.0 vol% fiber-reinforced composite group. When evaluating a regression equation, the coefficient of determination (R^2) represents 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 [59]. Using a calculated regression, R^2 for V_f explained 93% of the variation in modulus magnitude differences from the regression line (Fig. 1A). To better evaluate the correlation with modulus, by removing one group mean at 19.8 V_f , the regression line provided a better linear fit with all other group means at $R^2 = 0.9534$.

From a theoretical calculation perspective, the dominant factor for V_f can be emphasized to represent the ideal modulus from Eq. 14 at all rule-of-mixtures percentages and therefore R^2 would be 1.00. A modified rule of mixtures using the quartz fiber modulus of 78 GPa, Table 2, and the original 66 vol% particulate-filled composite experimental modulus value of 19.5 GPa by Eq. 14 is presented in Fig. 1B. Comparisons between the rule of mixtures and the experimental data, Fig. 1B, allow a simple evaluation for the efficiency of the discontinuous photocure fiber-reinforced composites. The least-squares line equation is linear and can be expressed by $Y = AX + B$ with Y the dependent variable modulus, X the independent variable for V_f , A being the slope, and B the intercept. The least-squares line equation then describes the minimum deviation linear relationship and can be used as a method to compare separate

regressions. Thus when comparing the ideal modulus rule-of-mixtures least-squares equation having an intercept identical to the experimental data at $0.0V_f$ with the experimental data least-squares line having experimental statistical deviations, minor differences on the order of about 0.5 GPa occurred at the intercept. These intercept differences between the least-squares lines were then accounted for in the EF determinations by a simple addition or subtraction correction term.

$$\text{Rule of mixtures regression } Y_{1\text{ROM}} = A_1X + B_1 \quad (18)$$

$$\text{Experimental regression } Y_{2\text{EXP}} = A_2X + B_2 \quad (19)$$

$$\text{Intercept term (IT)} B_2 - B_1 \quad (20)$$

$$\text{Rule of Mixtures EF regression } Y_{1\text{ROMEf}} = A_1X + B_1 + IT = A_1X + B_2 \quad (21)$$

A ratio evaluation between the dependent variables Y for modulus considers the experimental data and the rule-of-mixtures EF regression with a modified intercept. For the analysis, the right sides of the regression Eqs. 19 and 21, with X as the V_f independent variables, were compared. V_f was substituted into the experimental regression Eq. 19 for the numerator in the EF ratio with B_2 intercept. The rule of mixtures with the correction term in Eq. 21 was also used with the same V_f by replacing X to give the denominator in the EF ratio. With the same intercept, the regression lines only differed by their slopes.

$$\text{EFRatio} = Y_{2\text{EXP}} / Y_{1\text{ROMEf}} = (A_2V_f + B_2) / (A_1V_f + B_2) \quad (22)$$

The resultant experimental values derived from the least-squares line could then be directly compared with the values obtained through the theoretical rule-of-mixtures least-squares line (Table 6). EF ratios subsequently provided a range of values from $0.0V_f$ to $100.0V_f$. EF ratios thereby calculated include influences of all compounding variables other than V_f and would consist of resin-rich areas due to poor filler consolidation, voids, fiber crossovers, microcracks from cure stresses, debonding, fiber misalignment, fiber lengths, differences in fiber strength, fiber breakage, plastic strain constituent mismatches, and even test design.

Maximum flexural strengths increased from a mean of 117.6 MPa with the zirconia silicate particulate-filled composite group to 374.9 MPa at $28.2V_f$, and then leveled off to 421.3 MPa at $54.0V_f$ (Fig. 2A). Fiber volume percent R^2 calculations could explain 85% of the variability in flexural strength around the regression line. However, two separate material processes occurred with a transition at $28.2V_f$. Correlations between $0.0V_f$ to $28.2V_f$ and $28.2V_f$ to $54.0V_f$ provided R^2 values of 0.9255 and 0.2008 respectively. The initial $0.0V_f$ to $28.2V_f$ correlated well, while the latter $28.2V_f$ to $54.0V_f$ correlated poorly. Resin wetting of fibers was sufficient below $28.2V_f$. Above $28.2V_f$, resin impregnation may be the limiting factor reflected during plastic deformation where stress transfer was compromised between the polymer and increased number of fibers.

The rule of mixtures could similarly be compared for flexural strength, Fig. 2B, from Eq. 15 using theoretical yarn strength values from Table 2. EF ratio comparisons for strength are presented for different V_f fractions in Table 6.

The yield strength for the zirconia silicate particulate-filled composite was 95.4 MPa rising to 343.5 MPa at $28.2V_f$ and leveled out to 348.0 MPa at $54.0V_f$ (Fig. 3A). The yield strength demonstrated a similar increase compared to maximum flexural strength with the addition of fibers up to about $28.2V_f$ where the magnitude continued as a near horizontal plateau from $28.2V_f$ to $54.0V_f$. Correlations between $0.0V_f$ to $28.2V_f$ and $28.2V_f$ to $54.0V_f$ provided R^2 values of 0.8888 and 0.0069 respectively. The initial 0.0 to $28.2V_f$ concentrations correlate well with yield strength, while the latter $28.2V_f$ to $54.0V_f$ fiber fractions correlated so poorly that V_f could not explain any variability for yield strength.

The rule-of-mixtures regression for yield strength is presented in Fig. 3B with EF ratios in Table 6. The theoretical average quartz fiber yarn strength, and not yarn yield strength, was used for yield strength EF ratio calculations that would produce a somewhat higher rule-of-mixtures slope. So, such yield strength EF ratios might be slightly lower than expected, although they sufficiently correspond to flexural strength EF ratios.

Mechanical property deviations from linearity have been previously observed in fiber-reinforced composites due to porosity and fiber misalignment at higher fiber volume fractions [1, 60, 61]. Deviation from linearity above $28.2V_f$ for mechanical properties tested in this investigation could similarly be related to porosity due to insufficient polymer for fiber stress transfer while fiber misalignment is a second possibility that might be considered. Since the modulus is defined within the elastic material limits regarding isostrain, material flaws or discontinuities would not be expected to be critical. Experimental modulus values show high correlation, consistent with the rule of mixtures. As constituent strain mismatches increased during plastic deformation, nonideal properties became more readily accentuated and shear forces between separate material entities became more of a factor seen with both maximum flexural strength and yield strength. In addition, yield strength was calculated not only as a measure of the elastic strength limit, but was also a check on elastic modulus limit to help reduce variability during mechanical evaluation.

Altogether, V_f included as the rule of mixtures explained a significant proportion of variability about the regression lines for modulus, flexural strength, and yield strength. The correlation coefficient (R) is another measure of the influence for a linear relationship [59], for example, between V_f and a mechanical test variable. Fibers dominated properties so extensively that not only was the fiber fraction, V_f , highly correlated with modulus, flexural strength, and yield strength, but all mechanical properties correlated with one another through a random correlation matrix analysis at $p < 10^{-9}$ (Table 7).

From the correlation matrix when testing fiber-reinforced materials, a single measured property for modulus, flexural strength, or yield strength should provide basic screening comparisons for the other mechanical test variables. Flexural strength has typically been used as a general property to predict other mechanical characteristics and has been shown to be a good predictor for fatigue strength as well [62]. Predictors for fatigue strength might

also practically be expected with yield strength as a mechanical estimator for component service-life toward maintaining stress levels below the elastic limit.

The EF ratio appeared to be a good model by considering the dominant factor of V_f to explain nonideal test results due to all compounding variables when compared with theoretical predictions by the rule of mixtures. For simplicity regarding the EF ratios, the regression lines in Figs. 1B, 2B, and 3B provided easily identifiable comparisons between experimental results relative to the theoretical rule of mixtures. Experimental results for modulus defined within the elastic region of the load–deflection curve compared closely with the theoretical rule of mixtures. However, flexural strength and yield strength experimental results, measured in relation to permanent deformation, could not compare as well to the theoretical rule of mixtures. The EF ratios using the ultimate fiber properties as the uniform standard characterized the percent of all possible variables that reduced experimental results not explained by V_f at any fiber concentration. As V_f increased, EF ratios were sequentially reduced for all mechanical properties (Table 6). Starting with EF ratio values of 1.00 at the intercept for all three mechanical properties, all EF ratios then immediately became smaller and subsequently lower progressively in less significant increments. Loss of theoretical properties with progressively increasing fiber volume fractions characterized by the EF ratio produced a nonlinear curve, where the EF ratios were derived between two lines having the same intercept. When considering the EF ratio, standard international units should be used to maintain uniformity for comparative purposes as the intercept will influence the final ratios.

The EF ratio term was one consideration for the evaluation of specific fiber-reinforced composite systems, different composite processing techniques, or results from different laboratories. The regression EF appeared particularly appropriate for analysis in systems such as composites where fibers dominate the mechanical properties with corresponding high correlations. The regression EF ratio analysis provided a simplified means to compare correlations during composite development or as a part of continuing quality control. Since the EF ratio values followed a reverse relationship with V_f , analysis should not be restricted to comparisons with the overall mechanical properties at a specific V_f . EF ratios should further be considered in relation to the actual effectiveness of adding fiber reinforcement in relation to other compounding negative factors. For example, the economics for increased process costs should be contemplated in relation to the lower boundary of the EF ratio. So, EF ratios by the rule of mixtures with the regression line equation behave as a dual evaluation to give two separate analyses for properties and costs. General material property comparisons can include a range of V_f 's or any specific V_f up to 100 vol%, calculated from the regression lines. A more practical EF ratio economic consideration is for limiting returns on costs where negative factors can place a burden on the investment of adding fiber reinforcement. EF comparisons based on linear regression equations would further apply to correlation analysis by the rule of mixtures during development in other disciplines where optimum or maximum baselines can be standardized for comparisons with the sample population under study.

Particulate-Filled and Microfiber-Reinforced Composites

Representative load–deflection curves with samples of the same dimension are shown in Fig. 4 for comparison between the 66 vol% zirconia silicate particulate-filled composite and a composite with the same basic materials but with 28.2 vol% 3.0-mm quartz fibers. Improvements in mechanical properties characterized by the load–deflection curve for modulus, flexural strength, and strain with the addition of quartz fibers include areas under the curves indicative of enhanced static low strain rate toughness as resilience or work of fracture.

Regardless of the V_f above 0.0%, none of the 9.0 μm diameter, 3.0 mm length, fiber-reinforced samples failed by fracturing completely through the specimen material and all still supported a load at 5% deflection (δ) past peak force (Table 8). However, all zirconia silicate particulate-filled samples, Alert® samples with microfibers, and resin polymer samples broke completely through in brittle failure. Previous results have shown that 9.0 μm diameter quartz fibers with lengths of at least 2.0 mm or about $4L_c$ were necessary to increase the % load retained past peak force over particulate-filled composites at 28.2 V_f [13]. Similar fiber lengths were also required to significantly reduce crack propagation [13].

Mechanical property comparison controls for a commercial microfiber photocure composite and the neat photocure resin polymer are included in Figs. 1A, 2A, and 3A. Commercial photocure Alert® composite with approximately 26 vol% microfibers was not remarkable at any level tested. Particulate-filled composite with 66 vol% zirconia silicate filler with no fiber reinforcement showed increased properties compared with Alert® for all mechanical properties. The neat resin photocure polymer modulus increased significantly by adding 66 vol% zirconia silicate particulate filler or similarly when comparing Alert® photocure composite with radio-opaque silica filler and microfibers. Maximum flexural strength and yield strength for the neat resin polymer were comparable to those of the Alert®.

Interestingly, the rule of mixtures could be applied to 3M Corp. 66 vol% zirconia silicate spherical particulate-filled composite by the following equation [1, 63]:

$$\sigma_{yc} = \sigma_{ym}(1 + [L+t]/4L)V_p + \sigma_{ym}(1 - V_p) \quad (23)$$

where σ_{yc} is the predicted composite yield strength, σ_{ym} is the polymer matrix yield strength, V_p is the particulate volume fraction, L is the length of the particle perpendicular to the applied load, and t is the dimension of the particle parallel to the loading direction. Equation 23 simplifies for the case of the spherical zirconia silicate particulate to [1]

$$\sigma_{yc} = \sigma_{ym}(1 + 0.5V_p) \quad (24)$$

Accordingly, with an average polymer matrix yield strength of 52.5 MPa, the predicted composite yield strength is

$$52.5\text{MPa}(1 + [0.5][0.66]) = 69.8\text{MPa} \quad (25)$$

As a comparison, the average zirconia silicate particulate-filled composite test result was 95.4 MPa. When calculating individual theoretical yield strengths from the polymer by Eq. 25 compared with the experimental results with the zirconia silicate particulate-filled composite, results were significantly different $p < 0.05$. However, no account was taken for the zirconia silicate particles with uniform distribution sizes from 10 nm to 3.5 μm where van der Waals forces of attraction might improve the outcome. Compaction may also occur by improved packing fractions [2, 5] whereby weaker resin may be expressed away from the bulk composite and even squeezed from the mold at the surface during preparation as the top glass plates were clamped down.

Scanning Electron Microscopy

Samples chosen from the average modulus range for several V_f groups are shown in Figs. 5A–5J at 50 $\times$ and 200 $\times$ magnifications. These SEM images show that fibers exhibited a high degree of orientation with the long axis of the sample in relation to the four-point test span fixture. Similar alignments were seen at all V_f concentrations from 0.0 to 54.0 vol% toward meeting the requirements established by the theoretical rule-of-mixtures micromechanics. The sample at 5.4 V_f , Figs. 5A and 5B, was not sufficiently tough for parallel planar cleavage and instead broke in brittle fashion.

A representative sample for the commercial control composite Alert[®] is shown after the surface was stressed with a wear machine from a related study in Fig. 6. The SEM backscatter depth imaging for Alert[®] showed isotropic orientations with fibers much longer than the reported 40 μm , which has been previously imaged [64].

Fully Articulated Four-Point 40 mm Span Flexural Testing

A progressive design with high-tech materials was performed toward ideal flexural bend testing. 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 shearing effects. Subsequently, model test performance demonstrated correlations with extremely significant p values for the mechanical properties evaluated. By comparison using the same sample depths including 40 mm flexural span testing, similar test data using a shorter 20 mm fully articulated four-point span with an independent material analysis from the United States Department of Energy per modified ASTM standard for advanced ceramics ASTM-C-1161–94 [8, 22] is provided in Table 9.

A test span to sample depth ratio ($S:D$ ratio) less than 16 is considered too low to prevent load shear according to ASTM polymer standard D-6272–00 [53], which further recommends higher $S:D$ ratios for fiber-reinforced composites. Other researchers have previously indicated that $S:D$ ratios greater than 20 are necessary when testing fiber-reinforced composites [23, 24]. Shearing effects should therefore reduce both flexural modulus and strength values, which were found when comparing four-point differences between 20 mm and 40 mm span lengths. Shearing effects were further characterized by general fracture patterns that initiated toward one loading nose rather than at midspan where cracks then tended to deflect laterally toward the opposite loading nose for a majority of the fiber-reinforced composites. Shear fracture patterns were also the general feature for fiber-

reinforced samples during the United States Department of Energy testing [8] and later when testing different fiber lengths [13].

With regard to the four-point 40 mm span test modulus for the isotropic zirconia silicate particulate-filled composite formulated to simulate Z100[®] by 3M Corporation with an experimental static flexural average of 19.5 GPa, dynamic modulus measurements by resonance frequencies have produced slightly higher results of 20.9 GPa for Z100[®] [65]. Also, the Alert[®] modulus average using the 40 mm span length at 17.6 GPa could be compared again to dynamic modulus measurements of 18.5 GPa [66]. Dynamic modulus measurements unaffected by mechanical shearing were thus slightly higher than static flexural modulus measurements using a *S:D* ratio of 20 for both Z100[®] and Alert[®], which suggested that ratios greater than 20 might be necessary even when four-point flexural testing isotropic polymer matrix composites. Dynamic modulus measurements were also independently tested by Grindosonic (St. Louis, MO) providing results of 23.2 ($\pm$ 1.28) GPa for Z100[®]. Slightly higher values than reported in literature for the Z100[®] dynamic modulus might represent a careful uniform sample preparation to ensure minimized void content characterized by SEM with a sample chosen closest to the mean Izod toughness during the Department of Energy testing (Fig. 7) [8, 22]. Regardless, shear error might still be evident when four-point flexural testing isotropic particulate-filled polymer matrix composites using a *S:D* ratio of 20. Concerning dynamic resonance oscillatory deformation testing as a shear-free method, the ASTM Index 2001 for Mechanical Properties-Plastics uses only dynamic methods that include measurements for elastic modulus.

Fiber-Reinforced Photocure Molding Compound Applications

Significant research and development improvements for particulate-filled photocure zirconia silicate composites were shown with respect to mechanical properties when adding fiber volume percentages starting at 5.4V_f. Manufacturing processes for particulate-filled composites should be adaptable to low fiber concentrations toward an overall goal of replacing amalgam alloy for dental fillings. In addition to increased mechanical properties, fibers can be used to control compound handling. As a result, several clinical features may be improved that facilitate placement by the dentist [8, 22, 28]. When fully compounded with particulate filler, fibers allow packing techniques similar to the amalgam alloy, thereby minimizing the occurrence of large voids previously seen with particulate-filled dental composites [8, 22, 27, 28]. As underlying mechanical properties improve and as the fiber lengths increase beyond the average plowing groove to increase sheltering of both polymer and particulate filler, wear is expected to decrease [67–69]. Presently, the American Dental Association has not advocated use of particulate-filled composite in “stress bearing” areas [26]. However, when noting higher fiber volume percentages with strengths in the 400 MPa range, photocure fiber-reinforced composites may compensate for large losses of tooth structure, especially due to the adhesive stress transfer nature of the resin polymer matrix.

Nonthermal photocure processing which can be designed to eliminate dangers of thermal tissue necrosis is feasible for medical structural applications such as replacing chemical cure acrylic during cranioplasty. Photocure compounds are also practical toward improving contour adaptation for cranio-maxillo-facial fixation devices. In addition, nonthermal

processing can allow compound delivery with mineral and pharmaceutical release [70] or alternatively be used as high-tech structural encapsulants for microelectronics. The original particulate-filled composites were developed as bondable materials so that fiber reinforcement increases adhesive structural capability and has been shown to increase crack deflection [13]. As a result, difficult machining for multiple precision attachments using epoxy/carbon fiber composite superstructures under research and development can be adapted easier by completely filling in wider access openings down to flush zero tolerances at all contacts using a bondable crack-resistant photocure fiber-reinforced molding compound.

Investigating fiber-reinforced composite micromechanics in the region above critical aspect ratio provided practical test results for applications specifically intended for small component devices. In addition, with regard to an adhesive composite, larger structural repairs combined by bonding fiber-reinforced molding compound with epoxy/carbon fiber composite stiffeners and photocure woven fabric provide new avenues for material development. The ability to preimpregnate fiber-reinforced composites with photocure resins allows repairs to be made easily even in the field with low energy availability requirements. Nonthermal photocuring was employed as a means to also reduce thermally induced cure stresses during micromechanical analysis. However, other broad applications for fiber-reinforced molding compounds or fiber-reinforced bonding adhesives with insufficient visible-light access are also considered for curing by thermal or chemical means [13]. Structural adhesive bonding with fiber-reinforced adhesive molding compounds should then further help reduce use of strength-reducing fastener holes when bonding mainframe sections [32, 33].

SUMMARY

1. The initial research focus was toward commercial development of a molding compound for small, intricate spaces using fibers sufficiently long and added into a particulate-filled composite for vastly superior material properties. However, costs were a primary concern where micromechanics could be used to detail the economics while better understanding the science at the same time.
2. Isostrain conditions fundamental to the derivation of the rule of mixtures can be better appreciated when comparing theory to experimental results. Isostrain was thus emphasized throughout the simple derivation of the rule of mixtures in Eqs. 1–9 from beginning to end and helped to explain differences between modulus and strength results relative to elastic and permanent deformations.
3. Fiber influences on composite material properties showed that V_f could be used to explain a significant proportion of the variability for modulus, flexural strength, and yield strength at 93, 85, and 78% respectively.
4. Significant improvements with the addition of fibers began at 10.3 vol% for modulus, 5.4 vol% for flexural strength, and 10.3 vol% for yield strength, $p < 0.05$.

5. Correlation matrix analysis revealed that each mechanical property correlated significantly with V_f and all mechanical properties also correlated significantly with one another (all $p < 10^{-9}$).
6. The rule of mixtures practically demonstrated error not explained by V_f using EF ratios through least-squares correlation equation comparisons between experimental data. The EF ratios using the ultimate fiber property as the uniform standard will then characterize that percent of all possible variables which reduce experimental results not explained by V_f at any fiber concentration.
7. Model test methods using advanced ceramic articulated fixtures to reduce parallelism error, combining sufficiently long test spans to minimize load shearing effects, vinyl ester photocure resin to eliminate thermal stresses, vinyl ester resin compatible silane coupling with 99.99% silica pure quartz fibers, and uniform multimodal particle distribution for filler consolidation to lower void content aided in providing classic micromechanical rule-of-mixtures test data results for a bondable molding compound.

CONCLUSION

Mechanical property measurements versus the dominate factor for fiber volume percentages described a significant amount of the experimental variability for modulus, flexural strength, and yield strength. Micromechanics describing geometry arrangements with mechanical properties through V_f could thus be used to explain a majority of the mechanical properties through the rule-of-mixtures interpretation. Experimental test results for modulus were especially accurate compared to the rule of mixtures, since measurements were calculated from the elastic region of the load– deflection curve. SEM imaging showed that the fiber alignment was sufficient to produce results consistent with the rule-of- mixtures considerations. A photocure molding compound with 3.0-mm quartz fibers was capable of advancing several important mechanical properties when compared with particulate-filled photocure dental composites. An extension of discontinuous fiber-reinforced photocure composites was expected for several nonthermal ambient-cure applications for cranio-maxillo-facial reconstruction and microelectronic encapsulants, in addition to rapid field repair with structural bonding capabilities. Fiber volume percentage related mechanical improvements were also available during research and development as a measure to accommodate fiber scale-up with existing polymer or particulate- filled composite manufacturing equipment and packaging.

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NOMENCLATURE

EF	Efficiency Factor
L_c	Critical Length
L_c/d	Critical Aspect Ratio
p	Probability of Error when Claiming a Research Hypothesis
V_f	Fiber Volume Percent.

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(a)

(b)

FIG. 1.

(A) Group mean modulus for different fiber volume percents, $N = 4$. (B) Modulus EF analysis based on the rule of mixtures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(a)

(b)

FIG. 2.

(A) Group mean flexural strength for different fiber volume percents, $N = 4$. (B) Flexural strength EF analysis based on the rule of mixtures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(a)

(b)

FIG. 3.

(A) Group mean yield strength for different fiber volume percents, $N = 4$. (B) Yield strength EF analysis based on the rule of mixtures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 4.

Experimental data load-deflection curve comparisons for 0.0 and 28.2 vol % fibers.

Following maximum load, the immediate sporadic data points reflect the rapid force release during fracture crack propagation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FIG. 5.

(A) 5.4 vol% fibers, SEM $\times 50$ magnification, scale bar 500 μm . (B) 5.4 vol% fibers, SEM $\times 200$ magnification, scale bar 100 μm . (C) 10.3 vol% fibers, SEM $\times 50$ magnification, scale bar 500 μm . (D) 10.3 vol% fibers, SEM $\times 200$ magnification, scale bar 100 μm . (E) 19.8 vol% fibers, SEM $\times 50$ magnification, scale bar 500 μm . (F) 19.8 vol% fibers, SEM $\times 200$ magnification, scale bar 100 μm . (G) 28.2 vol% fibers, SEM $\times 50$ magnification, scale bar 500 μm . (H) 28.2 vol% fibers, SEM $\times 200$ magnification, scale bar 100 μm . (I) 54.0 vol% fibers, SEM $\times 50$ magnification, scale bar 500 μm . (J) 54.0 vol% fibers, SEM $\times 200$ magnification, scale bar 100 μm .

FIG. 6. Alert® commercial particulate-filled composite with microfibers from related wear testing, backscatter SEM $\times 200$ magnification, scale bar 100 μm .

FIG. 7. Z100® commercial particulate-filled composite following Izod fracture, $\times 40$ magnification, scale bar 500 μm .

TABLE 1

Mechanical properties for discontinuous thermosets (2000 – 2005).

Polymer	Composite fiber type	Fiber length (mm)	Vol% or wt%	Flexural strength (MPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Tensile modulus (GPa)
VE photocure [13]	Chopped quartz	2.0	30 wt%/28.2 vol%	373.9 ± 29.9		34.0 ± 2.9	
VE [37]	Glass mat	6.0–9.0	38–43 vol%		108.5 ± 18.6		15.0 ± 2.39
VE [37]	Glass mat	~25.0	38–43 vol%		193.4 ± 7.8		15.1 ± 1.3
UP [37]	Glass mat	6.0–9.0	38–43 vol%		107.0 ± 15.6		16.1 ± 2.1
UP [37]	Glass mat	~25.0	38–43 vol%		168.8 ± 21.0		14.9 ± 1.1
VE/EP [38]	Ceramic/glass mat	50.0	70 wt%	145.3 ± 4.1		6.4 ± 0.01	
SMC resin [39]	Chopped glass	25–50		70–160		7–11	
UP [40]	Chopped hard glass	50.8	21 vol%		100 ^a		
UP [40]	Chopped soft glass	50.8	21 vol%		85 ^a		
UP [40]	Chopped carbon	50.8	21 vol%		50 ^a		

VE, vinyl ester; SMC, sheet molding compound; UP, unsaturated polyester; EP, epoxy.

All mechanical properties are the maximum reported values.

^a Approximated from chart.

TABLE 2Properties of quartz fibers^a.

	Mechanical properties			
	Tensile strength (Mpa)	Flexural strength (MPa)	Tensile modulus (GPa)	Flexural modulus (GPa)
Virgin filament	6,000		78	
Yarn	1,500		78	
Unidirectional composite		1,200		35

^aDensity 2.2 g/cm³.

TABLE 3

Compound formulations volume percentages.

Weight percent (3.0 mm fibers)	Volume percentages			
	V_f	Vol%		
		Quartz fibers	Zirconia silicate	Bis-GMA TEGDMA
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
Densities (g/cm ³)	2.2	3.1005	1.14	1.07

The Alert[®] fiber volume fraction was estimated at ~26 V_f .

TABLE 4

Rheology comparisons regarding particulate and fiber compound.

	Fibers	Particulate	Resin
Less resin flow	Barrier effect	van der Waals forces of attraction	Higher viscosity; secondary bonding
More resin flow	Extra pressure	Spherical ball bearing effect	Lower viscosity; more diluent monomers

TABLE 5

Sample size estimate.

Wt% of fibers	Test	α	Power	Sample size
7	Flexural strength	0.05	0.9	3
8	Flexural strength	0.05	0.9	2
35	Flexural strength	0.001	0.95	2
35	Flexural modulus	0.01	0.9	3

TABLE 6

Fiber volume percent efficiency factors.

Fiber vol%	Modulus	Flexural strength	Yield strength
0	1.00	1.00	1.00
5.4	0.96	0.8	0.75
10.3	0.94	0.71	0.65
19.8	0.90	0.62	0.57
28.2	0.88	0.58	0.52
35.8	0.87	0.56	0.51
42.8	0.85	0.54	0.49
54	0.84	0.52	0.47
100	0.81	0.48	0.44

TABLE 7Correlation coefficient matrix analysis (p values), $N = 32$.

Variable	Volume fiber percent	Modulus	Flexural strength	Yield strength
Volume percent	1.000000	0.962555(10^{-17})	0.923391(10^{-13})	0.881697(10^{-10})
Modulus	0.962555(10^{-17})	1.000000	0.905629(10^{-11})	0.862895 (10^{-9})
Flexural strength	0.923391(10^{-13})	0.905629(10^{-11})	1.000000	0.967082(10^{-18})
Yield strength	0.881697(10^{-10})	0.862895 (10^{-9})	0.967082(10^{-18})	1.000000

TABLE 8

% Load retained at 5% δ past maximum force ($N = 4$).

Fiber volume percent	% Load ^a
0.0	0.0 (0)
5.4	27.0 (22.8)
10.3	48.8 (22.9)
19.8	28.4 (39.2)
28.2	70.3 (16)
35.8	87.0 (8.7)
42.8	58.9 (20.9)
54.0	76.5 (22.6)
0 (Photocure polymer)	0 (0)
0 (Alert composite)	0 (0)

^aValues in parentheses represent standard deviations.

TABLE 9

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

	20 mm span (<i>S:D</i> ratio 10, <i>N</i> = 10)		40 mm span (<i>S:D</i> ratio 20, <i>N</i> = 4)	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
84.5 wt% Zirconia silicate commercial	13.7	64.4		
35 wt% 3.0 mm quartz fibers added	19.8	227.2		
84.5 wt% Zirconia silicate prepared fresh			19.5	117.6
30 wt% 3.0 mm quartz fibers added			31.7	374.9

 $p < 0.001$ all comparisons between 20 mm and 40 mm test spans (*t*-test unequal variances).