EFFECT OF DIFFERENT PERCENTAGES OF SILICA NANOFIBERS FILLER LOADS ON MECHANICAL AND PHYSICAL PROPERTIES OF FLOWABLE COMPOSITE RESINS

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BIOMATERIALS

ABSTRACT

Dental composites are important in the spectra of restorative materials. Ability to match the color of natural dentition is an appealing characteristic of composite restorations. Additionally, they can be bonded physically to the tooth, which limits the amount of tooth preparation required and thereby conserves healthy tooth structure. In relation to other restorations like amalgams, non–metallic compositions of dental composites have exhibited good biocompatibility. The dental composites are composed of a resin matrix containing a blend of bis-GMA (bis-phenol A-glycidyldimethacrylate) or urethane dimethacrylate (UDMA) along with TEGDMA (tetraethylglycidylmethacrylate). Novel techniques for the reinforcement of these resin-based composites continue in a research and development phase, since the existing resin-filler systems may not be suitable for long term applications in large restorations. The nanofillers reinforced composite resins had shown promising results. Silica-based nanoparticles and clusters are blended with larger-sized fillers and are available commercially for restoring large posterior restorations. These nanoparticles, offer poor crack blunting ability due to their shape and very small diameters and also improves the stiffness of the composites. However, addition of fibers, by virtue of their geometry and very large aspect ratios, may provide better resistance to fracture. The objective of this
study was to study the effect of silica nanofiber (SNF) and a mixture of Silica filler particles (SFP) reinforcement on the fracture toughness, flexural strength, three body wear, polymerization shrinkage, rheology, gloss and degree of conversion of bis-GMA/TEGMA based composite resin.

Silica nanofibers (SNF) were fabricated using electrospinning and incorporated 20wt %, 35.8wt% and mixture of 20 wt% of SNF and SFP in ratio of 1:1 (20wt% H), into a bis-GMA/TEGDMA matrix. Experimental groups composed of clear resin and traditionally filled flowable resin (PermaFlo, Ultradent) were tested as negative and positive controls respectively. Data were analyzed using one way ANOVA and Tukey’s test. Experimental group with 20 wt% of SNF and SNP mixture showed highest fracture toughness, flexural strength, wear resistant, degree of conversion. 20wt% showed highest gloss and 35.8wt% showed best rheological properties. Significant increase in all tested properties (p<0.001) was seen after addition of nanofiber.
DEDICATED:

To my parents, brother, sister-in-law, fiancée and my mentor Dr. John O. Burgess
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 OBJECTIVES</td>
<td>15</td>
</tr>
<tr>
<td>3 NULL HYPOTHESIS</td>
<td>16</td>
</tr>
<tr>
<td>4 LITERATURE REVIEW</td>
<td>17</td>
</tr>
<tr>
<td>4.1 Dental Caries and Restorative materials</td>
<td>17</td>
</tr>
<tr>
<td>4.2 Dental Composites</td>
<td>18</td>
</tr>
<tr>
<td>4.2.1 Based on Dimension.</td>
<td>22</td>
</tr>
<tr>
<td>4.2.2 Based on Material.</td>
<td>23</td>
</tr>
<tr>
<td>4.2.3 Based on Geometry.</td>
<td>24</td>
</tr>
<tr>
<td>4.4 Fabrication of Nanofibers</td>
<td>24</td>
</tr>
<tr>
<td>4.4.1 Drawing</td>
<td>25</td>
</tr>
<tr>
<td>4.4.2 Molecular Self–Assembly</td>
<td>26</td>
</tr>
<tr>
<td>4.4.3 Template Synthesis</td>
<td>26</td>
</tr>
<tr>
<td>4.4.4 Phase Separation</td>
<td>27</td>
</tr>
</tbody>
</table>
4.4.5 Electrospinning ........................................................................................................27

5 MATERIALS ..................................................................................................................32
  5.1 Electrospinning solution ............................................................................................32
    5.1.1 Sol Precursors .................................................................................................32
    5.1.2 Binder Polymer ...............................................................................................33
  5.2 Experimental Groups .............................................................................................34

6 METHODS ......................................................................................................................35
  6.1 Fabrication of SNF .................................................................................................35
    6.1.1 Preparation of Silica Sol ................................................................................35
    6.1.2 Electrospinning ...............................................................................................36
    6.1.3 Calcination ......................................................................................................37
  6.2 Characterization of Nanofibers .............................................................................38
    6.2.1 Scanning Electron Microscope (SEM) ............................................................38
    6.2.2 Fourier Transform Infrared Spectroscopy (FTIR) ..........................................38
    6.2.3 X-Ray diffraction ...........................................................................................38
  6.3 Silanization of Fibers and Sample Preparation .......................................................39
    6.3.1 SNF Incorporation into Dental Resin ...............................................................40
  6.4 Characterization of Experimental Groups ............................................................40
    6.4.1 Rheology .........................................................................................................40
    6.4.2 Gloss ...............................................................................................................41
    6.4.3 Degree of Conversion (DC) ...........................................................................42
    6.4.4 Polymerization Shrinkage ..............................................................................43
    6.4.5 Wear Testing ...................................................................................................44
6.4.6 Fracture Toughness and Flexural Strength .............................................. 47

7 RESULTS AND DISCUSSION ............................................................................. 51

7.1 Characterization of Nanofibers .................................................................... 51

7.1.1 Scanning Electron Microscope (SEM) ...................................................... 51

7.1.2 Fourier Transform Infrared Spectroscopy (FTIR) and Energy dispersive
spectroscopy (EDS) ............................................................................................... 55

7.1.3 X-Ray Diffraction (XRD) ........................................................................... 56

7.2 Characterization of SNF reinforced composite resin ....................................... 57

7.2.1 Rheology ........................................................................................................ 57

7.2.2 Gloss ................................................................................................................. 58

7.2.2 Degree of Conversion (DC) ........................................................................ 59

7.2.3 Polymerization Shrinkage ............................................................................ 61

7.2.4 Wear Testing ................................................................................................... 62

7.2.5 Fracture Toughness and Flexural Strength .................................................. 65

8 NULL HYPOTHESIS REJECTION ..................................................................... 71

9 CONCLUSIONS .................................................................................................. 72

LIST OF REFERENCES .............................................................................................. 74
LIST OF TABLES

Table Page

1 Filler loading and filler size distribution in different composite systems [38]................14

2 Represents 3 experimental groups with different filler loads (wt%) and Clear Resin and PermaFlo (Negative and positive control respectively).........................31
# LIST OF FIGURES

*Figure Page*


2. Classification of tooth colored restorative materials .......................................................... 3

3. The effect of high polymerization shrinkage (a) and low polymerization shrinkage (b) on the bond between restoration and the tooth ........................................ 7

4. Chemical structures of (a) bis-GMA and (b) TEGDMA ........................................... 19-20

5. Represents the silicon bridging between the polymer matrix and inorganic fillers .......................................................... 21

6. Chemical structure of γ-mercaptopropyl-trimethoxysilane ........................................ 21

7. Schematic depicting the augmentation in packing fraction with different sizes of fillers ................................................................................. 23

8. Schematic of continuously drawn array of fibers on a silicon substrate adapted from the work done by Nain et al [77] ........................................ 25


10. Schematic of the electrospinning apparatus [84] ...................................................... 28

11. Chemical structure of tetra (ethyl orthosilicate) (TEOS) ........................................ 33

12. Molecular structure of Polyvinylpyrrolidone (PVP) .................................................. 34

13. Depiction of technique for preparing the silica sol. HCl is added drop-by-drop to the ethanol, TEOS and distilled water blend, followed by a heat treatment .......... 36

14. Schematic of the electrospinning apparatus consisting of a syringe with polymer solution, high voltage source attached to the needle tip and a grounded static aluminium collector .......................................................... 37
15 Diagrammatic representation of X-Ray diffraction Technique [103]………………...39

16 Specifications of a parallel plate rheometer in oscillatory mode......................... 38

17 The ACUVOL showing the rotating pedestal for sample placement

   and camera for real time imaging.................................................................44

18 (a, c) Composite specimen build up incrementally using hand instruments,
(b) light curing the final layer of the composite specimen under a glass slide,
(d) mounted specimen (center) on brass holder, (e) polishing of the
mounted specimens and (f) the Alabama wear simulator .....................................46

19 Proscan volumetric shrinkage machine with samples placed for scanning .............47

20 Specimens dimensions and applied loads in a fracture toughness test...................48

21 Systematic representation of three point bend test...........................................49

22 Represents silica nanofibers (a, b) produced at 20 wt% precursor solution.
   Uniform diameter fibers were observed. No bead or droplet formation
   was observed..............................................................................................52

23 (a,b) represents SNF after calcinations at 4000x and 14,000x..............................53

24 Represents silica nanofibers diameter distribution before (PVP-SNF) and
   after calcinations (SNF-C).............................................................................54

25 Represents FT-IR spectrum comparing calcinated and un-calcinated
   silica nanofiber............................................................................................55

26 XRD of SNF with peak at 2θ angle of 21º shows amorphous silica......................56

27 Represents change in viscosity of different experimental groups
   (20wt%, 35.8wt% and 20wt% H) compared with unfilled and highly
   filled (PermaFlo) composite resins...............................................................58

28 Represents comparison of mean and SD gloss values of all tested groups..............59

29 Represents comparison of degree of conversion among tested groups (Mean±SD)…59

30 Degree of conversion was measured by comparing absorption peaks of
   aliphatic C=C (1638 cm⁻¹) and aromatic C-C peaks (1608 cm⁻¹) using equation 5…..60
31 Represents comparison of polymerization shrinkage percentages and standard deviation values of all experimental groups (Mean±SD).....................62

32 (a,b,e,f) represents superimposed scans generated using PROFORM software in which, top surface represents pre-wear surface and bottom image represents post-wear image of all groups 20wt%, 35.8wt%, 20wt% H and Permaflo respectively. (c,d,g,f) represents wear pattern observed in all groups in same order as mentioned above.................63

33 Comparison of volumetric loss (mm$^3$) among all experimental groups (Mean±SD).................................................................64

34 Comparison of $K_{IC}$ values (with Standard deviations) for all 5 tested groups (Mean ± SD)........................................................................65

35 SEM images of fractured surfaces: (a, b) clear resin specimens with distinct ridges formed due to a brittle fracture, (c) PermaFlo specimen with areas of irregular cleavages.................................................................67

36 Shows distribution of various filler loads and fracture pattern in 20 wt% (a), 35.8 wt% (b) and 20 wt% H (c). Arrows in a) indicates fiber pull out and SNF projected from resin matrix and crack propagation. Arrows in b) represents fracture pattern and projected SNF from resin matrix. Arrows in c) represent fiber pull-out, non uniform distribution of SFP.................68
1 INTRODUCTION

Dental caries is one of the world’s most common diseases which is affecting approximately 80% of the developed countries population [1]. As per the report by U.S. department of health and human services, in United States, dental caries is a most common chronic childhood disease, diagnosed at least five times more frequently than asthma [2]. Management of carious teeth is necessary and it follows a multilevel approach, comprising early interventions, such as topical fluoride application, to more aggressive treatments including the replacement of lost tooth structure by restorative measures. Dental wear, abrasion, erosion of tooth structure, trauma are some other reasons for the placement of dental restorations. Based on dental insurance claim data, in the year 2005, an estimated total of 166 million restorations were performed in the United States alone [3]. This increased demand for dental restorations has encouraged researchers to search for innovative and superior dental restorative materials.

The spectrum of dental restorative materials has widened considerably since the treatment was first practiced several millennia ago. During Egyptian civilization, gold wire, ox bone and wood were often used as tooth replacement materials. Marco Polo et al mentioned the use of gold leaves as decoration on teeth in Chinese civilizations around 1280 AD [4]. During 14th century, a textbook named, Chirurgia Magna, was written by the famous French surgeon Guy de Chauliac, presented dental disease in a new perspective.
In 15\textsuperscript{th} century, Giovanni de Arcoli (Italy) introduced metallic restorations, such as gold foils, and was made popular as dental materials in 1728 by a French physician, Pierre Fauchard, when he started using gold as restorative material for filling teeth and making denture bases. Today, dental restorative materials are broadly classified into various categories- metal alloys, polymeric resins and ceramics.

Metallic alloys, such as dental amalgams, have been in use since the early nineteenth century. Amalgam technically means an alloy of mercury mixed with any other metal, however dental amalgam is an alloy of mercury with silver-tin amalgam alloy. The longevity of dental amalgam in posterior restorations had been well established with a survival rate of 80% according to a 12.5 year clinical study [5]. The most accepted explanation for the longevity of dental amalgam restoration is the leaching of corrosion products from these restorations which further seals the tooth-restoration interface. This seal prevents further the microleakage of bacteria and bacterial products into the tooth structure and eliminates subsequent damage from dental caries. Additionally, dental amalgam restorations have also exhibits a similar wear rate as of the natural dentition. However, with increasing demand of tooth colored restorations and reports of mercury toxicity has led to the steady decline in their popularity.

With the increasing demand tooth colored restorations led to the emergence of composite resins in 1962, after R.L Bowen developed the bis-GMA (bisphenol–A-glycidyl methacrylate) resin matrix. Along with resin matrix, these composites also consisted of inorganic fillers, such as radio-opaque glass, quartz, or ceramic particles. Initially, their use was confined to aesthetics governed area like anterior teeth, however, with the increase in preference for tooth-colored restorations, among dentists and patients, use of resin composites has increased [6, 7] as seen in Figure 1.
Fig. 1. The market share of type of dental restorations placed in the United states in the year 2005 [3].

Compomers, glass ionomer cements, composite resins and ceramics are widely used tooth-colored restorative materials today. As observed in Figure 2, each class of tooth colored restoration is further sub-categorized based on the modifications included in the composition of the base material.

Fig. 2. Classification of tooth colored restorative materials.
Among tooth colored restorative materials, composite resins, glass ionomer cements and compomers are used as direct restorations and have shown acceptable durability in smaller tooth preparations [8]. However, studies have shown that with improved control over filler composition and loading and filler-matrix chemistry, has led to significant improvements in the properties of these composite resins [9].

Studies have shown that these dental composite resins can be successfully used in Class I (one missing tooth wall) and Class II (two missing tooth walls) restorations [10]. Collins et al found that the average annual failure rate of a posterior composite restoration is about 1.2 % during 8 year follow up [11], with wear rates ranging between 7 - 12 µm/yr [9]. Studies also show that dental cements reinforced with resins have also shown acceptable durability in restoring Class I and II cavities in primary teeth [12].

The primary constituents of the resin matrix are resin monomers and an initiator/catalyst system for polymerization. In spite of improvements in resin composites, material limitations exist which restrict the use of resin composite as a posterior restorative material. Clinically, resin restorations are difficult and require more placement time than a similar sized amalgam restoration [13]. Interproximal contacts are difficult to obtain since composite is a paste material that shrinks during polymerization.

The initiator/catalyst system for direct RBC may be chemically or light activated. With chemically activated polymerization, benzoyl peroxide is the initiator and a tertiary amine, e.g., dihydroxyethylparatoludine (DHEPT) or sulfonic acid initiator is the activator [14]. Once the two paste chemically-cured RBC is mixed, the initiator and activator contact and polymerization begins. After a few minutes the polymerization produces a gel (solid) where the polymer is cross linked enough to form a cohesive mass which may
be finished and polished. In the 1980's visible light-cured (VLC) resin-based composites were introduced to the dental profession. These resins systems became very popular and now are the dominant, directly placed esthetic material.

Visible light-cured RBCs are single paste materials polymerized with visible light energy. VLC RBC allow the operator to control setting time; require no mixing, have fewer voids, greater strength, greater fracture toughness; better shade selection, improved color stability and higher polymerization conversion rates than chemically activated RBC. VLC RBC polymerizes by free radical polymerization. Visible light-cured RBC has a photo-initiator and accelerator/catalyst system for polymerization. The photoinitiator absorbs light energy (photons) emitted from the curing light and directly or indirectly initiates polymerization. Photoinitiators are diketones, such as camphoroquinone, activated by visible light, in the presence of an amine accelerator/catalyst, e.g., dimethylamino ethylmethacrylate (DMAEM). The activated diketone/amine complex initiates the polymerization of the dimethacrylate resin monomers. VLC RBC contains a lower concentration of amine accelerators than chemically cured RBC; which increases the color stability of VLC RBC compared to chemically activated RBC [15-17]. Camphoroquinone is a commonly used photoinitiator with major absorption of visible light wavelengths in the 460-480 nm (blue) range. RBCs may contain a combination of photoinitiators, each requiring its own specific wavelength for maximum reactivity. Camphorquinone has a maximum absorption spectrum of 468 nm, which is close to the peak spectral output of the LED curing lights [18]. Since different composite resins have different photoinitiators, the wavelength of light absorbed by the photoinitiator for maximum polymerization should be provided for
each composite [19]. Percent conversion or the ratio of double bonds converted to single bonds indicates the extent of polymerization. Composites with higher percent conversion have greater mechanical properties, wear resistance, better color stability and are more biocompatible which contributes to maximum restoration longevity [20].

During polymerization of resin-based composite the distance between the monomers decreases as the carbon atoms bond together and molecular movement decreases. With present day RBCs this shrinkage ranges from 1.5% to 3.0% per volume. Composite resin placed in a cavity preparation is confined by the preparation. Shrinkage of the composite resin transfers stress to the cavity walls. Polymerization shrinkage can tear the adhesive bond from the tooth [21], or pull the opposing cusps together by deforming the tooth depending upon the thickness of the remaining tooth [22]. Shrinkage of the RBC can fracture the marginal tooth structure, tear the adhesive or cause tooth structure to deform which increases microleakage, postoperative sensitivity, staining and recurrent caries (Figure 3). Increasing the filler content of RBC minimizes resin content and reduces the shrinkage, and increases the stiffness or (modulus of elasticity). The magnitude of the contraction stress is related to the cavity configuration [23], the compliance of the composite and the surrounding tooth structure [24] the composite resin degree of conversion and the conversion rate of the composite which is related to the modulus of the composite [25]. As RBC polymerizes, the amount of stress generated to the surrounding tooth depends in part upon the rate of modulus development. High modulus composites with rapid conversion rates transfer stress to the surrounding tooth structure more rapidly than lower modulus materials with slow conversion rates.
Another significant limitation of these materials is a chipping fracture that occurs commonly in larger restorations. Improved mechanical properties may be obtained by varying filler size and shape, volume fraction loading, composition of the resin matrix and filler-matrix interfacial bonding [26]. Silanization of silica filler particles improves filler-matrix bonding and increases mechanical properties of commercially produced composites [27].

Since the introduction of dental resin-based composites as posterior restorative materials, their clinical behavior has been determined by their mechanical properties [28]. During the ‘70s and ‘80s the main failure mechanisms of composite restorations were...
insufficient wear resistance, loss of anatomic form, and degradation of the restoration [29]. The improvement in filler technology resulted in more wear resistant composites and changed the failures improving composite restoration performance [30]. Wear can cause tipping of the occlusal plane (a plane passing through the occlusal or biting surfaces of the teeth), leading to imbalances in the transmission of forces to the temporo-mandibular (jaw) joints. Over the years, this may lead to chronic inflammation of the joint space, restricting jaw movement. Wear of composite restorations in particular adversely affects their esthetics. An increased amount of staining and loss of gloss is associated with composite wear surfaces.

Generally, increased filler volumetric percentage (filler loading) improves the physical and mechanical properties of RBC. Most filler particles are silicon dioxide based and are either: crystalline silica--quartz; silica with metals--silicate glass; or amorphous silica--colloidal or fumed silica. Fillers vary in size from a distribution that averages less than 0.1 um to a distribution that averages 10 to 100 um [31]. Wear resistance of composites improved with the addition of increased volume filler loading and filler particle size distribution, unfortunately these newer materials became more brittle, increasing the occurrence of bulk fractures [28]. A fracture within the body of restorations and at the margins is a major failure mechanism of posterior composites. The fracture related material properties, such as fracture resistance, elasticity, and the marginal degradation of materials under stress have usually been evaluated by measuring flexural strength, flexural modulus and fracture toughness of the developing materials [32]. The presence of filler particles in restorative materials substantially increases the
fracture toughness and the toughening mechanisms are assumed to be crack pinning, crack deflection and matrix–filler interactions [33, 34].

Resin-based composites mechanical properties are dependent upon their microstructure and composition. The microstructural characteristics involve the distribution of filler particles in the monomer matrix, the morphology of these filler particles and the presence of pre-existing cracks and voids. The inorganic filler content and bond to the monomer matrix are most significant factors improving the mechanical properties of resin-based composites [35]. Mechanical properties of the composite resin increase with greater filler volume fraction while polymerization shrinkage decreases [25]. Smaller filler particles have a more pronounced effect on strength than larger particles at the same volume fraction [36]. Kim et al. observed a significant influence of the filler rate and morphology on the flexural strength and modulus, microhardness and fracture toughness of the composites resin [37]. Ikejima et al reported that the increase in mechanical properties stopped when the filler load was 50%/vol [36].

Filler-matrix interfacial bonding that is achieved by silane coupling agent, is another contributing factor in increasing mechanical properties of commercially produced composites. Silane bonds the fillers to the matrix. Silanization of silica filler particles is a well established method for increasing the silica filler-matrix interfacial bonding [27]. Vallittu [38] studied the influence of 2 silane compounds on the adhesion between denture base acrylic and different types of fiber, including glass fibers. The silanized glass fibers used for reinforcement markedly increased fracture resistance. In another study, the importance of filler silanation was clearly demonstrated, as flexural strength, flexural modulus and shear strength of the composites with silanated fillers were
significantly higher than those of the composites with un-silanated fillers [36]. The incorporation of nanometric sized filler particles in hybrid composites and even the introduction of exclusively nanofilled composites are the most recent advances in filler technology. Characteristically, these filler particles, due to their small size and rounded shape, expose a high surface area and require, as a consequence, a higher amount of silane. Musanje and Ferracane reported that the incorporation of silanized nanofiller particles significantly increased abrasion and attrition wear resistance of an experimental hybrid composite [27]. The same authors also reported that silanized nanometric filler particles are capable of increasing the flexural strength and microhardness of composites.

All commercial composites have limitations either they have significant strength or poor esthetics and lack gloss retention. Gloss is a physical property that is used to describe the reflectivity of the composite surface. Reflectivity gives RBCs a more life like esthetic appearance and is achieved by polishing the restoration. The polish of a resin composite surface is related to the intrinsic properties of the material as well as the finishing/polishing procedures used. With heterogeneous materials, such as composite resins, smoothness of restorations is influenced by the filler size (macrofill, microfill, microhybride, nanofill, and nanocluster filler), type of filler (silica or zirconica/silica) and the filler arrangement.

Nanoparticles improve mechanical properties of materials. In dentistry, posterior restorations (fillings) require resin composites with high mechanical properties while anterior restorations where less bite force is exerted require resin composites with superior esthetics and polish retention. Due to the reduced dimension of the particles and a wide size distribution, an increased filler load can be achieved which reduces
polymerization shrinkage while increasing the mechanical properties [39]. Small filler particles improve the optical properties of resin composites because their diameter is less than the wavelength of visible light (0.4-0.8 µm), resulting in the human’s eye inability to detect the particles making the composite appear smoother [40].

The wear resistance of composite resins is significantly improved with decreased average filler particle size and with increased filler loading [41]. Higher wear rates are related to the larger filler particles in the composite materials [42]. Therefore, having high filler content with small average filler size has been a method to produce composite resins for posterior restorations, which need an adequate strength and wear resistance to withstand the mastication forces, especially in highly stressed fillings [43]. The fillers themselves, the filler load level and the filler–matrix-interactions have a greater influence on fracture parameter of dental composites than the structure of the organic matrix. The average filler size and the filler volume greatly affect the wear properties of the composite materials.

Fiber reinforcement has been successfully used in dentistry for indications where polymers have performed well, such as complete dentures and provisional restorations [44]. Incorporation of fiber into dental polymers has been shown to enhance mechanical properties [45-48]. Fiber reinforcement of polymers increases modulus of elasticity and toughness via “modulus transfer”. Modulus transfer generally involves high elastic modulus fibers in a lower elastic modulus matrix. A stress applied to the composite is “transferred” from the matrix to the fibers. This transfer requires a reasonable level of bond or friction between the fibers and matrix.
Several factors control the degree of toughening that can be achieved by modulus transfer: difference in modulus between the fiber and the matrix, strength of the fibers, volume fraction of the fibers and architecture of the fiber contribution, length of the fibers and interfacial bond between the fibers and matrix. The volume fraction of fibers that can be successfully incorporated into a matrix affects the toughness and strength achieved in that composite. Large volume is desirable as long as the fibers don’t interact in such a way that they are damaged and lose strength. The resin impregnation is more difficult at higher volume fractions (fiber volume fraction higher than 50%); while the fiber distribution is less uniform at low-volume fractions [49]. Unidirectional fibers provide toughening and strengthening only in the direction parallel to the fibers (one dimensional architecture). Strength and toughening in the other directions are no better than for the matrix. Such composites often fail in interlaminar shear rather than in tension. To increase the resistance to shear failure, fibers are built into the composite additional directions. Multidirectional architectures result in a decreased number of fibers in any angle direction, so that the strength in the strongest direction is not as high as for unidirectional fibers. However, the strength in the minimum direction is increased for three-dimensional and higher composites to yield improved resistance to failure by interlaminar shear mode.

Fiber length also affects the toughening and strengthening capability of fibers in a composite. Modulus transfer can occur with shorter “chopped” fibers, but achieving a controlled architecture or distribution of chopped fibers is difficult. The minimum length of fiber that will yield modulus transfer depends on the relative moduli of the fiber and matrix and on the degree of bonding between the fiber and matrix. Fiber diameter also
found to have an influence in reinforcement. Griffith recorded a strength value of approximately 100 MPa for bulk glass, but as he drew the fibers to smaller diameters, their strength increased dramatically [50].

Ongoing research designed to reinforce composites has shown that the addition of nanofillers in dental resins leads to enhanced wear resistance, improvement in mechanical properties and polymerization mechanics. In addition, a noticeable improvement in the polishability and surface gloss of these materials has been observed after nanofiller reinforcement [51]. The nanofillers used typically are silica and zirconia nanomers (20 nm) and nanoclusters (3 - 5 µm) [52]. While these nanofilled hybrid materials have shown improvement in mechanical properties, they rarely show effective crack resistance [52]. This current study employs reinforcement of silica nanofibers in dental resins. Nanofibers are polymeric or ceramic fibers having diameters ranging from 50 - 500 nm by virtue of which they have a high surface area and possess many desirable properties for reinforcement of polymers [53]. Along with their usage in advanced applications such as bone and tissue scaffolds, drug delivery and catalyst enzyme carriers, nanofibers have also been used for reinforcing other thermosetting resins namely epoxy and elastomers such as rubber [54]. Kenig et al. have reported that micron scaled glass fibers and nanofibers made of nylon 6, polyvinyl alcohol and Poly-L-Lactic acid reinforce dental composites and have increased the fracture resistance of bis-GMA based composites [55, 56].

Short and networked carbon fibers have been used experimentally to increase mechanical properties of resin composites. However carbon whiskers are difficult to bond to the resin matrix. Xu et al. demonstrated that whiskers mixed into composite without
silica particles became entangled and dispersion in the matrix was difficult [26]. In addition, fusing silica particles onto the whiskers enhanced the whisker silanization and its bonding to the resin matrix indicating whiskers cannot be silanated, furthermore, whiskers impart a dark black color to the composite making it unaesthetic limiting patient acceptance.

Recently, silica nanofibers have been successfully processed and offer a promising reinforcement alternative to polymeric fibers because of the improved bonding between silica and the resin matrix that can be achieved using a silane-based coupling agent [57, 58]. Silica-filled composites also have the added advantage of improved esthetics due to a similar refractive index to tooth.

In this study, after incorporating silica nanofibers (SNF) into a flowable composite resin, the mechanical material properties of this formulation were measured and compared to the unfilled flowable resin and commercially available highly filled flowable composite resin.

The organization of this thesis is as follows. A description of objectives, three specific aims of this research, null hypothesis is followed by the summary of relevant literature and a background to the challenges encountered in current resin-based dental restorative materials. The Materials and Methods follow the review section and describe the experimental design, materials used, processing method, testing, and characterization techniques employed in this study. The Conclusion highlights major outcomes, practical implications, and limitations of this work.
2. OBJECTIVES

The objective of this study was to fabricate silica nanofibers and blend them with commercially available resin monomer to form highly reinforced direct filling flowable composite resin with improved mechanical and physical properties. The three specific aims of this study are as follows.

☐ Silica nanofibers (SNF) fabrication, heat treatment and characterization of SNF using scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy and X-Ray diffraction (XRD).

☐ Surface treatment of nanofibers and incorporation of nanofibers in resin matrix in different filler loads.

☐ Testing and compare the mechanical and physical properties of the experimental composite groups produced by adding different percentages of SNF filler loads.
3. NULL HYPOTHESIS

No difference will be observed in the mechanical and physical properties of flowable composites produced by adding different filler load, compared with unfilled composite resin and highly filled flowable composite resin.
4. LITERATURE REVIEW

Organization of this section is as follows: background information regarding dental diseases and need for a dental restoration, followed by a detailed review of the dental composite resins composition, their clinical benefits, advantages and disadvantages as well as challenges encountered by clinicians and manufacturers in optimizing their handling characteristics and mechanical properties. The different types of filler reinforcements used in dental composites and the benefits of each filler reinforcements on basis of size and shape are discussed. Based on information gathered from literature review and the available techniques, materials selection and methods of silica nanofiber fabrication as a means of reinforcement are then studied, and an experimental design is prepared and presented in sections 5 through 6.

4.1 Dental Caries and Restorative materials

According to the survey done by National Institute of Dental and Craniofacial Research, dental caries is one of the most common chronic diseases in children [2]. Dental caries is defined as a destructive process causing decalcification of mineralized tissues of the tooth, i.e enamel, dentin and cementum and results in cavitation of tooth. Dental caries occurs when acid releasing bacteria colonize the tooth surface. *Streptococcus mutans* and *S. sobrinus* are cariogenic bacteria that are part of the normal flora of the oral cavity [59] and these microorganisms can be isolated from the plaque
surrounding the dentition. Normal pH of saliva is in the range of 6.5 to 7.4. However, demineralization of enamel begins with increase in concentration of acid released, and the saliva attains a pH of 5.5 or less. These sequences of events can be observed soon after the consumption of a carbohydrate rich meal, which are easily fermented by bacteria present in saliva. Inadequate or poor oral hygiene allows *Streptococcus mutans* and other cariogenic bacteria to multiply and colonize the tooth. These bacteria secrete lactic acid as a byproduct after carbohydrate metabolism, creating a surface demineralization which further results in a cavity, if not arrested results in pulpal inflammation and periapical pathology with loss of tooth vitality. Once the caries has established in the tooth structure, removal of the carious tooth structure followed by a dental restoration can prevent its further spread. A timely intervention to restore the weakened tooth back to its structure and function prevents the onset of new lesions in contacting teeth in the opposing as well as same arch [58]. An ideal dental restorative material should have properties similar to tooth and would be esthetically acceptable, biocompatible, wear resistant, fracture and fatigue resistant [58]. With the development of awareness among people towards oral hygiene and measures such as better health care, water and milk fluoridation, and improvement in the diet of developed countries have also reduced caries prevalence [2].

4.2 Dental Composites

Dental composite resins were first introduced commercially in 1962. These are tooth colored restorative materials, and are available in various shades and translucencies to match natural tooth color. Additionally, they can be bonded to the tooth, limiting the amount of tooth preparation required in metallic restorations and thereby conserving
healthy tooth structure. Bond between the dental composite resin and tooth structure also helps in distributing stresses generated during mastication more uniformly which further supports the remaining weakened tooth structure [58].

A dental composite is commonly composed of fillers like quartz, silica, glass fillers, organic resin and photoinitiators [59, 60]. The resin matrix is typically composed of bis-GMA (bis-phenol A-glycidyldimethacrylate), Urethane dimethacrylate (UDMA), bis(methacryloyloxymethyl)tricyclodecane. Bis-GMA is the most commonly used resin in majority of the dental composite resins marketed today, since it shows a relatively small percentage of polymerization shrinkage and stress post polymerization. However, the structure of bis-GMA, as seen in Figure 4 (a), makes it extremely viscous, which further reduces the degree of potential reinforcement to the matrix for improving its stiffness.

To reduce the viscosity of bis-GMA and to improve the handling properties of dental composite, a low molecular weight monomer TEGDMA (tetraethylglycidylmethacrylate), (Figure 4(b)), is blended with bis-GMA in varying percentages. Unfortunately, addition of TEGDMA results in increased polymerization shrinkage of the system.
Increased polymerization shrinkage creates a corresponding stress at the marginal interface, leading to de-bonding of the restoration, marginal staining and secondary caries in the marginal gap. Hence, a correct ratio of the percentages of the competing resins is critical to the final properties of the composite.

Addition of fillers in resin reduces polymerization shrinkage by substitution of the resin matrix by volume. Additionally, they also improve required mechanical properties such as fracture toughness, flexural strength, modulus, wear resistance and decrease water sorption [8]. There are various inorganic fillers used in dental composites which are typically glass, quartz, barium silicate, zirconium silicate, barium, strontium etc. A small percentage (5 – 10%) of pre-polymerized resin commonly referred to as “organic” filler is also added in microfilled composites. The fillers are treated with silane coupling agent to establish a chemical bond between fillers and with the resin matrix and to improve dispersion of fillers within resin matrix. Literature shows that the interfacial treatment of inorganic fillers with a silane coupling agent affects the mechanical properties of the resulting composite [61, 62]. Further studies have shown that improved mechanical properties were more significant with silane treated fiber reinforced composites compared with silane treated particles reinforced composites [63].

Fig. 4. Chemical structures of (a) bis-GMA and (b) TEGDMA
Silane coupling agents are mostly organo-silane compounds with two different reactive groups bonded to the silicon atom as seen in Figure 5. While at one end, for example the hydroxyl group, reacts with the silica in inorganic fillers such as glass to form a chemical bond; the reactive groups at the other end (e.g. vinyl, epoxy, methacryl, amino and mercapto groups) bond with various kinds of organic materials or synthetic resins to form a chemical bond. Figure 6 shows a commonly used coupling agent in dental composites is $\gamma$-mercaptopropyl-trimethoxysilane.

Fig. 5. Represents the silicon bridging between the polymer matrix and inorganic fillers

Fig. 6. Chemical structure of $\gamma$-mercaptopropyl-trimethoxysilane
Studies had also shown that silane treatment of nano-filled composites affects thermal characteristics of dental composites [64]. A shift in glass transition temperature (Tg) of the composite is observed with reinforcement of silane treated fillers. This holds an important implication to the performance of dental restorative materials, since on an average the mouth undergoes a temperature variation from 5.6 to 58.5 °C in a 24 h period [65]. Hence, the application of the coupling agent is vital to controlling the properties of the composite. A detailed discussion of the varieties of fillers used in dental composites is presented in Section 4.2.1 through 4.2.3.

4.2.1 Based on Dimension.

Dental composites are classified on the basis of type of fillers they contain and viscosity (Table 2). Traditional composites, with filler size of 20 – 50 μm, produced restorations with poor polishability, high surface roughness and inadequate gloss retention [66, 67]. These defects resulted when the surrounding resin matrix wore under masticatory loads exposing large hard fillers, which ultimately protruded past the matrix. Microfilled composites with micron-sized colloidal silica produced a smooth surface finish but had reduced properties compared to macrofilled composites [68].

Table 1. Filler loading and filler size distribution in different composite systems [69].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Filler Size (μm)</th>
<th>Filler wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional</td>
<td>1-50</td>
<td>60-70</td>
</tr>
<tr>
<td>Hybrid</td>
<td>0.4-1</td>
<td>60-65</td>
</tr>
<tr>
<td>Nanocomposite</td>
<td>0.002-0.075</td>
<td>78-80</td>
</tr>
<tr>
<td>Microfilled</td>
<td>0.04-0.4</td>
<td>32-50</td>
</tr>
<tr>
<td>Packable</td>
<td>0.04, 0.2-20</td>
<td>59-80</td>
</tr>
<tr>
<td>Flowable</td>
<td>0.6-1.0</td>
<td>42-62</td>
</tr>
</tbody>
</table>
Hybrid composites containing multiscaled “organic” (pre-polymerized resin) and inorganic fillers was introduced later in the market and these materials offered a compromise between esthetics and mechanical properties. Addition of multiscaled fillers (Figure 7) resulted in increased filler loading and also reduced polymerization shrinkage. With advancements in technology and the known benefits of the novel properties of nanosized fillers, nano-filled dental resins were introduced. Now a days, majority of posterior composite restorations are restored using nano-hybrids.

![Fig. 7](image.png)

Fig. 7. Schematic depicting the augmentation in packing fraction with different sizes of fillers.

4.2.2 Based on Material.

With the increasing interest of patients towards esthetic dentistry, dental composite should meet the demands of today’s restorative needs, and hence, dental composites need to match tooth color and translucency, necessitating an optical index close to 1.5. In addition to the improved esthetics achieved, if the refractive index of fillers matches that of the resin matrix, an increased depth of cure occurs due to enhanced light transmittance with light activated systems. As mentioned earlier, fillers such as strontium, barium, slass, silica, quartz, zirconia, borosilicate glass and pre-polymerized resin, are commonly in dental composites. Today, colloidal silica and pre-polymerized resin are the main fillers in the commercially available hybrid composites.
Fillers of various shapes like spherical or irregular shaped depending on the manufacturing method are used commercially. Each shape have their own significance like spherical fillers provide a tighter packing [70], whereas, fillers with sharp angulations can act as stress concentration sites, reducing fracture toughness of the composite [71]. In order to overcome stress concentration, carbon whiskers possessing a fibrous geometry were used to reinforce dental resins [72]. These long carbon fibers improved fracture toughness and modulus of the resin, and the long fibers improved the fracture toughness of the components [71, 73 - 75]. Glass fibers have also been used in perform inserts which are polymerized resin matrices containing embedded glass fibers [73]. The purpose behind this approach was to avoid challenges like fiber pullouts during polishing and wear and also addition of pre-cured composite in the restoration helps to reduce shrinkage. However, carbon whiskers imparted a black color to the composite, making it unesthetic, thus limiting patient acceptance, while glass fibers disintegrated from the matrix when subject to abrasion. Recently, micron-sized short fibers and nanofibers made of polymeric material have been used for improving composite strength and have shown promising results [55, 54]. Kenig et al. showed that addition of 5 % (w/w) neat nylon 6 nanofibers into bis-GMA/TEGDMA (50/50 mass ratio) improved work-of-fracture, flexural strength and elastic modulus compare to unfilled formulations.

4.3 Fabrication of Nanofibers

Since silica has shown many favorable properties and can be bonded to the resin matrix, we began an investigation into the various available sources and methods for fabricating silica nanofibers. Several techniques can be used for silica nanofibers
fabrication. Silica nanofibers can be fabricated using techniques such as drawing, template synthesis, temperature-induced phase separation, molecular self assembly, and electrospinning [76].

4.4.1 Drawing

Polymeric micro/nanofibers may be formed by drawing and solidification of a viscous liquid polymer solution, which is pumped through a glass micropipette or may be extracted using instruments as seen in Figure 8. This process facilitates the formation of networks of suspended fibers having amorphous internal structures. Using this method, individual fiber diameters up to 50 nm may be produced. The fiber drawing method, however, is limited by time, since the viscosity of the polymer solution increases while the volume of solution available in every drop decreases. This affects the quality and reproducibility of the fiber diameters [77, 78].

![Fig. 8. Schematic of continuously drawn array of fibers on a silicon substrate adapted from the work done by Nain et al [77].](image)
4.4.2 Molecular Self–Assembly

Molecular self–assembly involves the building of nano-sized structures such as colloids, nanotubes, and wires through chemical synthesis [79]. However, it requires complex procedures and techniques, and the diameter formed is in tens of nanometers. Such dimensions are too small to be effective reinforcement for improving the toughness of materials.

4.4.3 Template Synthesis

Template synthesis is a popular method for fabricating nanowires of conductive polymers, metals and semiconductors. Figure 9 shows the process of obtaining nanowires, by filling a porous template containing a large number of straight cylindrical uniform-sized holes. Two popular methods for filling the template are either by high pressure injection from a melt or by electrochemical deposition [80]. Fibrils as fine as 3 nm have been fabricated using this method; however, the overall fiber diameter distribution obtained is narrow [81]. Since the targeted diameter desired for the silica nanofibers is in range of 150 – 450 nm in order to achieve a high volume fraction, a method for fabricating nanofibers is required that can deliver fibers in a range of diameters.

Fig.9. Template Synthesis of Nanowire/Nanotube Heterostructures [82]
4.4.4 Phase Separation

Phase separation refers to the process of thermodynamic separation of polymer solution into polymer-rich/poor layers. It has been used effectively in the production of scaffolds, but has a drawback of small production scales. This method is still currently in use for production of biological scaffolds.

4.4.5 Electrospinning

Electrospinning is a popular technique to fabricate synthetic or biological polymers and ceramic nanofibers [83-90]. Originally, this technique was employed to make tissue scaffolds for bone and cartilage, but high strength composites, nanoporous membranes for filtration, drug delivery and enzyme carriers are also fabricated using the same methodology. The process has been in use for over 80 years and was first patented by Formhals in 1934. He designed an apparatus and electrospun cellulose acetate using an acetone/alcohol solution as the solvent. However, due to a close proximity of the collector to the charged polymer solution, the solvent did not evaporate completely. Later, a better understanding of the process helped researchers develop a more useful technique to produce continuous fibers whose diameters can be controlled by optimizing the experimental parameters.

The electrospinning apparatus, as depicted in Figure 10, uses a high voltage source, a syringe filled with polymer solution, and a grounded metallic collector. The solution to be spun is pumped at a low rate through the needle, forming a semi-spherical droplet shape at the needle tip. Applying high voltage to the needle introduces a charge in the solution. When the electrostatic forces become large enough to repel the surface tension, an elongated droplet at the tip known as the Taylor’s cone is formed and a jet is
ejected. Any instability in the electric field causes the jet to take a whipping motion which helps to stretch the fibers and evaporate any solvent [91].

The fibers can be electrospun either from melt or by the sol-gel technique. The sol-gel technique for the fabrication of silica fibers is the most commonly used approach, since it offers a high yield of silicon dioxide. Preference for the sol-gel technique to prepare the precursor solution also stems from the ease with which this process can be adapted for nanotechnology, by controlling the scale of production in contrast to the traditional melt-derived approach. The sol-gel approach allows for fiber diameters from 50 – 1000 nm, while the melt approach restricts the fibers in the 10 – 100 nm range [92]. In addition, the sol-gel approach yields a higher silica content per mole [93]. Once the sol is prepared, a binder polymer is incorporated to facilitate the charging of the solution and formation of smooth fibers.

The quality of fibers formed and the ability to spin uniform fibers with bead-free
morphology depends upon factors such as applied voltage, needle tip to collector distance, solution pump rate, solution concentration, viscosity and surface tension.

4.4.5.1 *Applied voltage.*

The morphology of the fibers is controlled by voltage. Varying the applied electric field can alter the fiber diameter. Both low and excessively high field strengths can lead to bead defects or even failure in jet formation, which leads to an interruption in fiber production. At low voltages, the Taylor cone forms in the tip of the pendent drop; however, as the voltage is increased the volume of the drop decreases until only the Taylor cone remains formed at the end of the capillary. Low voltages provoke the drop to oscillate with time [94]. At too low voltages, gravitational forces dictate the distortion in shape of the drop, ultimately resulting in dripping of the pendent drop. If the voltage is too high, the drop becomes smaller and the beginning of the jet shifts to the edge of the capillary’s orifice and finally stops [94]. After a certain minimum voltage is attained, fiber formation starts; low voltages yield beaded fibers and higher voltages yield smooth fibers. Nonetheless, increasing the voltage further will also produce beaded fibers. This increase in the density of beaded fibers is a result of the inability of a stable Taylor cone to form at high voltages and the consequent formation of an unstable liquid jet [83]. The average fiber diameter increases as the voltage is increased [83]. This probably happens due to a higher mass flow caused by the increased field strength.
4.4.5.2 Solution pump rate.

Polymer flow rate has an effect on fiber size, which can influence fiber porosity and fiber shape. It has been postulated that the polymer’s flow should be enough to replace the material ejected in the fiber jet. Generally, fiber diameter increases as the feeding rate increases. The enlarged diameter is due to the increased mass flow rate of the polymer solution. A mathematical model developed by Fridrick et al. validated that increasing the flow rate produces a six-fold variation in fiber diameter [95]. Another anomaly associated with high flow rates is the appearance of beads on the fibers which can be attributed to insufficient solvent evaporation before reaching the collector plate. Hollow tubes or ribbon like structures are also seen since sufficient time is available only for the outer surface to dry and solidify, leaving the inner core hollow. A collapse of these tubes later results in the band like flat ribbons being formed.

4.4.5.3 Tip to collector distance.

By adjusting the distance between the tip of the needle and collector plate, fiber diameter can be altered. An increase in this distance results in smaller diameter of fibers and reduction in appearance of beaded structures, since a larger distance allows for increased whipping motion of the polymer jet and thinning of the fibers [84]. Additionally, more time is available for the complete evaporation of the solvents in the solution before deposition of the fibers. The optimum distance however has to be maintained since a larger distance results in the gravitational forces overcoming the voltage.
4.4.5.4 *Viscosity of precursor solution.*

The solution should have a high enough polymer concentration to allow chain entanglements, yet low enough so that too high a viscosity does not prevent fiber formation [96]. The instability in the jet driven by its surface tension is the cause for the formation of beads [97]. At a higher concentration of solution, the entangled polymeric molecules need longer time to diffuse and relax [96, 98]. A certain amount of entanglements (elasticity) are however required to form uniform fibers. Hence, there is a fine interplay between viscosity and fiber formation. When the polymer concentration is too low (low elasticity), the jet breaks up into droplets and if it is too viscous, fibers will not be formed.

4.4.5.5 *Surface tension*

Surface tension is a result of the interplay between the solvent properties and the polymer concentration. Reduction in the surface tension of the polymer solution limits bead formation. Hence the choice of the solvent/polymer combination is critical to the spinnability of the solution and proper fiber formation [94].

Based on the above parameters the experimental design of the study was developed as described in the following section.
5. MATERIALS

This study was divided into 3 phases - nanofiber fabrication, preparation of experimental material and experimental composite testing. The nanofibers used in this study were fabricated by the process of electrospinning. Following fibers fabrication, fibers were surface treated with silane coupling agent before being incorporated into a base resin, which also contained a light activated curing agent. The following section provides a description of the materials that were employed in this study.

5.1 Electrospinning solution

Electrospinning involves a sol-gel technique for the preparation of a sol, which is blend with a polymer. A set of sol-precursors are mixed in a specific ratio and allowed to mature for 2 hours. A detail of the materials used for preparing the electrospinning solution is presented.

5.1.1 Sol Precursors

Three precursors were used for the electrospinning solution: tetra (ethyl orthosilicate), ethanol, and hydrochloric acid. Reagent-grade tetra (ethyl orthosilicate) (TEOS) with 98% purity was obtained from Sigma-Aldrich, Inc. TEOS is the ethyl ester of orthosilicic acid, Si(OH)$_4$ that is classified as an organo-metallic compound, i.e., it has
an organic ligand attached to a metalloid atom as seen in Figure 11 [99]. The reactivity of the Si-OR bonds makes it a widely used cross-linking agent in silicone polymers. This chemical compound Si(OC$_2$H$_5$)$_4$ was used in sol-gel synthesis of silicon dioxide through a hydrolysis reaction, as depicted in Equation 1, followed by a condensation reaction with water [100].

$$\text{Si(OC}_2\text{H}_5\text{)}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}$$ \hspace{1cm} [Equation 1]

Laboratory grade ethanol (C$_2$H$_5$OH) and 98 % HCl were obtained from Fisher Scientific, Pittsburgh, PA. Ethanol is a known organic solvent and is commonly used in the manufacture of silica by the sol-gel method. HCl was used to catalyze the sol-gel hydrolysis.

5.1.2 Binder Polymer

Poly (vinyl pyrrolidone) (PVP) is a synthetic polymer, which was used in the electrospinning of silica nanofibers. Figure 12 shows the chemical structure of PVP. The molecule acted as a binder and facilitated the formation of nanofibers in the electrospinning process. The ease of solubility of the polymer in water, and other polar
solvents accounts for its good wetting properties. For this study, PVP was purchased from Sigma-Aldrich Inc., with an average molecular weight of 55,000 and was used as received.

![Molecular structure of Polyvinylpyrrolidone (PVP)](image)

**Fig. 12. Molecular structure of Polyvinylpyrrolidone (PVP)**

### 5.2 Experimental Groups

The experimental groups were designed based on the matrix, filler type and percentage of filler content as seen in Table 2. For all resin groups, the same bis-GMA/TEGDMA ratio was maintained. Light activated initiators were added to render the experimental resins photo-polymerizable.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Matrix</th>
<th>Filler type</th>
<th>Filler wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear resin (Negative Control)</td>
<td>Bis-GMA/ TEGDMA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Experimental 1 (20wt%)</td>
<td>Bis-GMA/ TEGDMA</td>
<td>Silica nanofibers</td>
<td>20</td>
</tr>
<tr>
<td>Experimental 2 (35.8wt%)</td>
<td>Bis-GMA/ TEGDMA</td>
<td>Silica nanofibers</td>
<td>35.8</td>
</tr>
<tr>
<td>Experimental 3 (20wt% H)</td>
<td>Bis-GMA/ TEGDMA</td>
<td>Silica nanofibers &amp; nanoparticles</td>
<td>20 (1:1)</td>
</tr>
<tr>
<td>PermaFlo (Positive Control)</td>
<td>Bis-GMA/ TEGDMA</td>
<td>Macroparticles</td>
<td>68</td>
</tr>
</tbody>
</table>

Table 2. Represents 3 experimental groups with different filler loads (wt%) and Clear Resin and PermaFlo (Negative and positive control respectively).
6. METHODS

The first half of the study was dedicated towards the development of SNF. The electrospinning procedure, subsequent heat treatment procedures, and a detailed description of the characterization methodology employed for determining the quality of the SNF are provided in this section. The second half of the study was devoted to the characterization of the experimental composites. In this segment, the procedures for determining fracture toughness, flexural strength, three body wear, viscoelastic properties, polymerization shrinkage, degree of conversion and gloss of the bis-GMA resin-based experimental composite groups are explained.

6.1 Fabrication of SNF

6.1.1 Preparation of Silica Sol

Silicon dioxide was synthesized using an acid catalyzed sol-gel process in this study [56, 101, 102]. The sol was prepared using TEOS and ethanol in acidified water [57]. Figure 13 shows the acidic catalysis of the sol, initiated by the addition of HCl, which is known to produce linear structures in contrast to basic catalysis, which yields branched structures [57, 99].

The sol was allowed to stir continuously on a heated stirrer plate and cooled to room temperature. This maturation procedure was used to consolidate the linear structure of the silica molecules and to increase the viscosity of the sol.
6.1.2 Electrospinning

A horizontal electrospinning apparatus was used for fabricating the PVP-SNF (silica nanofiber) mats as reviewed in the literature represented in Figure 14. PVP powder was dissolved in silica-sol and ethanol under gentle agitation to obtain a solution with 20% wt/vol concentration. This mixture was allowed to stir for 2 h to obtain an optimum viscosity for electrospinning. The resulting solution was transferred into a 5 ml syringe with a 25½-gauge needle and electrospun at a voltage of 18 kV using a high voltage source (M826, Gamma High-Voltage Research, Ormond Beach, FL). The feeding rate of the polymer solution was set to 0.5 ml/h using a syringe pump (KD Scientific, Holliston, MA). The polymer solution jet ejected from the tip of the needle was collected at room temperature on a grounded rotating collector (5000 rpm) covered with aluminum sheet at a distance of approximately 20 cm. Random, non-woven mats were obtained.
6.1.3 Calcination

Calcination is a thermal treatment done to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. In order to remove the PVP binder molecules from the electrospun PVP-SNF mats, the mats were calcined. The mats were heated in a furnace (ProPress 100, Whip Mix Corporation, USA) was maintained for 2 hours. The calcined mats were allowed slowly to cool to room temperature. Non-woven silica nanofiber mats (SNF-C), devoid of any binder polymer, were obtained.
6.2 Characterization of nanofibers

6.2.1 Scanning Electron Microscope (SEM)

SEM (FEI Company Quanta 650 FEG) was used for determining fiber morphology of uncalcinated silica nanofiber (PVP-SNF) and calcinated silica nanofiber (SNF-C) mats. Samples were sputter-coated with Au-Pd under vacuum and examined at an accelerating voltage of 20 kV at the upper stage position. Fiber diameter measurements were calculated using SEM micrographs of both PVP–SNF and SNF-C mats by Image Analyzer software (Image-J, Image Processing and Analysis in JAVA). A hundred counts per micrograph were made.

6.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy (NICOLET 4700 Thermo Electron Corporations, USA) was used to analyze the silica nanofiber before calcification (PVP-SNF) and after calcification (SNF-C) in attenuated total reflectance (ATR) mode. Each specimen was configured to have 32 scans per minute at a resolution of 4 cm⁻¹. The resulting spectra were used to determine the molecular structure and estimate the amount of PVP present in the sample before and after heat treatment.

6.2.3 X-Ray Diffraction (XRD)

X-Ray diffraction (Siemens D500 Diffractometer) was used to characterize the crystallographic structure of calcinated silica fibers. This technique is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in a system (Figure 15).
A rotating X-ray generator (40 kW, 40 mA) with Cu Kα radiation (wavelength $\lambda = 1.54$ Å) was used for XRD measurement. The XRD profiles were recorded from 0° to 60° at a scanning speed of 2°/min. The resulting diffraction pattern was used to characterize the crystallographic structure of calcinated silica fibers.

6.3 Silanization of Fibers and Sample Preparation

A surface treatment to the SNF was done by Ultradent Products, Inc., (Salt Lake City, Utah, USA). The purpose of surface treatment of SNF was to improve bonding between the matrix and silica nanofibers. The silanated fibers were processed to powdery consistency before incorporation into resin matrix.
6.3.1 SNF Incorporation into Dental Resin

The silanized SNF were incorporated in photo-polymerizable bis-GMA/TEGDMA matrix under high vacuum and shear mixing at Ultradent Products Inc (Salt Lake City, Utah, USA). A filler loading of 20 wt% and 35.8 wt% of nanofibers was used to prepare experimental group 1 and 2 respectively. A third experimental group was prepared by incorporating a mixture of SNF and spherical silica filler particles (SFN) (diameter 1µ) in ratio of 1:1 and filler load of 20 wt% using similar procedures and base resin as the SNF group.

6.4 Characterization of Experimental Groups

6.4.1 Rheology (Visco-elastic property)

Rheological properties of all experimental resins were determined for the assessment of their handling properties and their ability to adapt cavity walls during restoration of cavity. Visco-elastic property was also determined to study the effect of nanofiber incorporation on the viscosity of the uncured composite. All experimental groups were tested using a parallel plate (diameter = 25 mm) fixture of the Rheometer (AR 2000, TA Instruments, New Castle, Delaware USA). Figure 16 shows a representation of the instrument fixture with the distance between the plates fixed at 0.5 mm. Strain sweeps employed 0.01-100.0% strain at a shear rate of 1.0 s⁻¹. A frequency sweep was performed at 25°C.
6.4.2. Gloss

Tooth-colored resin composites have been widely used because of their excellent esthetic properties [104, 105]. Surface roughness, surface gloss, and color are among the most important factors in the perceived visual effects of resin composite restorations [106]. Gloss is an aspect of the visual perception of objects that is as important as color when considering the psychological impact of products on a consumer. It has been defined as ‘The attribute of surfaces that causes them to have shiny or lustrous, metallic appearance’. Five specimens (Dimensions 10x6x2 mm) per group were prepared. Each specimen was cured for 20 seconds using 3M Elipar S10 (Power Intensity: 1000-1100 mW/cm²), polished with SiC abrasive paper (320-600-1200-2000) under water spray for 1 minute each using a rotational polishing device (No 233-0-1997, Buehler Ltd, Evantson, IL) followed by finishing with 0.05 µm alumina slurry and a polishing cloth. Specimens were rinsed under water and ultrasonically cleaned in an ultrasonic unit (Branson 1200) in distilled water for 5 min. Prepared specimens were stored in deionized water for 24 hours at 37°C before measurement of gloss. Gloss for all the experimental
groups were measured by glossmeter (Rhoptoin Nano-curve Glossmeter). This instrument is based on ASTDM D 523 specification. Gloss was measured on a scale of 1 to 100 with a square measurement area of 2x2 mm and 60° geometry. One reading was made, specimen rotated at 90° and another reading made. The mean of two readings was recorded as gloss unit (GU) of a specimen.

6.4.3. Degree of Conversion (DC)

The percentage degree of conversion (DC) was calculated using spectra from a FT-IR spectrometer (NICOLET 4700 Thermo Electron Corporations, USA) that used an attenuated total reflectance crystal (ATR). The composite specimens were prepared with dimensions (d=10mm, t=2mm). The specimens were light cured using 3M ESPE Elipar S10 (Power Intensity: 1000-1100 mW/cm²), and stored at 37 °C for 24 h before testing. For all experimental groups, spectra for uncured and cured (24 hours post cure) samples were obtained using the FT-IR with the same operating parameters as mentioned in section 6.2.2.

The degree of conversion of dental composites is the conversion of monomer to polymer after curing and is measured in term of concentration of reacted double bonds as a percentage of the total amount of methacrylate groups present in the unpolymerized resin. Bis-GMA based resin systems consists of two very prominent absorbance peaks; 1638 cm⁻¹ corresponding to C = C bonds stretching in the aliphatic ring and 1608 cm⁻¹ corresponding to the C – C stretching vibrations of aromatic rings. Aromatic peak intensity is considered as an internal standard and remains unaffected by double bond conversion occurring during polymerization. The remaining double bonds for each spectrum was determined by a comparison of the aliphatic C = C peaks with the standard.
Equation 2 was used to calculate the DC [107, 108].

\[
DC = 100 \left( 1 - \frac{\left( \frac{C_{\text{C = C_aliphatic}}}{C_{\text{C = C_aromatic}}} \right)_{\text{cured}}}{\left( \frac{C_{\text{C = C_aliphatic}}}{C_{\text{C = C_aromatic}}} \right)_{\text{uncured}}} \right)
\]  

[Equation 2]

Where:

C = C Aliphatic corresponds to absorbance peak 1638 cm\(^{-1}\)

C = C Aromatic corresponds to absorbance peak 1608 cm\(^{-1}\)

6.4.4 Polymerization Shrinkage

Polymerization shrinkage represents difference in volume of a material before and after curing and is measured as percent change in volume. Polymerization shrinkage was determined using ACUVOL volumetric shrinkage analyzer (BISCO, Inc., Schaumburg, IL) (figure 17). ACUVOL uses a video imaging technique to measure volumetric shrinkage. Several other methods had been used in past to measure shrinkage such as mercury dilatometry, water dilatometry, strain gauge, linear contraction, and density measurements [109-114]. However, use of mercury in mercury dilatometry procedure [115] raised health concerns which limit its use whereas, use of other procedures do not possess the ease of operation that the ACUVOL provides. Additionally, the linear contraction and density measurement methods are not applicable to all situations, particularly specimens involving anisotropic structures.

Specimens of all experimental groups were placed on the pedestal in the
ACUVOL chamber as small spheres and cured for 20 s after placing using 3M ESPE Elipar S10 (Power Intensity: 1000-1100 mW/cm²). The shrinkage values were recorded continuously for about 10 min after curing. The average of the values between 7 min and 10 min intervals was used as the final shrinkage value because these percent shrinkage values were observed to be near-steady. Five readings were taken for each material. A one-way ANOVA and Tukey/Kramer test was done to determine any difference between the experimental groups tested.

![ACUVOL chamber](image)

**Fig. 17.** The Acuvol showing the rotating pedestal for sample placement and camera for real time imaging.

**6.4.5 Three Body Wear Testing**

The Alabama wear simulator, an in vitro model for wear measurement, was employed for testing four experimental resin groups. *In-vitro* models have proved to be useful tools in the measurement of wear of dental materials [116]. These *in-vitro* models provide standardized testing conditions by controlling variables such as force, acidity of the environment, exposure time, temperature, provides ease of studying wear at an accelerated rate. However, the ability to simulate the biological condition of the oral cavity in its entirety is the biggest drawback of *in-vitro* wear stimulators. The *in-vitro*
dental wear simulators cited in dental literature consist of the Oregon Health Sciences University Oral Wear Simulator (OHSU), University of Alabama at Birmingham Wear Simulator, Zurich computer controlled masticator, BIOMAT wear simulator, ACTA wear machine and Minnesota MTS wear simulator. The University of Alabama at Birmingham wear simulator has been cited the most out of all the available systems [100].

The Alabama wear simulator consists of a stylus with replaceable tips (stainless steel, ceramic or composite). Each stylus uses springs to generate a force of approximately 75 N, which is calibrated separately for each stylus/sample pair. Studies have shown that clinically relevant biting forces range from 20 – 120 N [100, 117]. Alabama wear stimulator design permits four samples to be mounted on brass holders with acrylic that are fastened opposing the stylus.

The five experimental composite resin groups were tested for wear properties. Figures 18 (a) through 18 (e), show the different steps in the preparation of the wear samples. Samples (n=8) were prepared using cylindrical mold made of an impression material with the dimensions of d = 10 mm and h = 4 mm, was used to prepare eight composite samples for each material. The composite specimens was built up in 2 increments, 2 mm each and were light cured using 3M ESPE Elipar S10 curing light (Power: 1000-1100 mW/cm²), for 20 seconds. The prepared specimens were stored in de-ionized water at 37 °C for 24 h following which they were embedded in the center of brass holders (d = 15 mm) using a self curing acrylic material. Specimens were wet ground flat using 320, 600, 1200-grit SiC abrasive paper under water spray for 1 min each, using a rotational polishing device (Model No: 233-0-1997, Buehler Ltd, Evanston, IL, USA) followed by finishing with 0.05 µm alumina slurry and a polishing cloth. They were rinsed under water and cleaned with an ultrasonic bath in distilled water for 5 min.
Fig. 18. (a, c) Composite specimen build up incrementally using hand instruments, (b) light curing the final layer of the composite specimen under a glass slide, (d) mounted specimen (center) on brass holder, (e) polishing of the mounted specimens and (f) the Alabama wear simulator

The prepared specimens were then placed in the Alabama wear simulator, as shown in Figure 18 (f). A load of 75 N was applied using stainless steel tips for 200,000 cycles. PMMA beads (d = 50 µm) were mixed with water (15 g beads for 9 g water) and
made into a paste. Prepared paste was introduced between the specimens and the stylus as a third body media. A non-contact 3D surface measurement instrument (PROSCAN 2000, Scantron Industrial Products, Ltd., Taunton, England) was used to scan the specimens (figure 19). The volumetric wear and depth of wear of the materials was determined using ProForm software (Scantron Industrial Products, Ltd., Taunton, England). One-Way Anova and post-hoc Tukey’s Kramer test was used for data analysis.

6.4.6 Fracture Toughness and Flexural Strength

Fracture toughness specimens (n=10) of all five experimental groups were prepared using a Teflon mold with dimensions of $25 \times 2 \times 2$ mm, with a 1 mm notch at 12.5 mm (Figure 20). The specimens were light cured (3M ESPE Elipar S10) overlapping previous cured areas on the exposed surfaces of the specimen for 20 s. Specimens were stored in deionized water at 37°C for 24 h and then fracture-tested using 3-point bend technique on the Instron 5565 (Universal Testing Machines, Admet, Norwood, MA) at a cross head speed of approximately 1 mm/min.

Fig. 19. Proscan volumetric shrinkage machine with samples placed for scanning
Fig. 20. Specimen dimensions and applied loads in a fracture toughness test

The stress field around the notch in the specimens is described by term, $K_I$ (stress intensity factor). The notch which is a representative of a crack, grows when the stress field reaches to a critical value, i.e., at critical $K$, also known as $K_{IC}$ (fracture toughness). Peak failure load was recorded for each experimental group, and $K_{IC}$ values were calculated using Equation 3.

$$K_{IC} = \frac{PLF(x)}{bw^{1.5}}$$  \hspace{1cm} [Equation 3]

Where

- $P$ = Fracture load
- $b$ = thickness of specimen
- $w$ = width of specimen
- $L$ = span of base;
- $F(x)$ = Constant; function of location and length of crack

Flexural strength specimens ($n=10$) were prepared using a Teflon mold with dimensions of $25 \times 2 \times 2$ mm. The specimens were light cured (3M ESPE Elipar S10) at three overlapping areas on the exposed surfaces of the specimen for 20 s. The prepared
specimens were stored in deionized water at room temperature for 24 h and then fracture-tested using 3-point bend technique (Figure 21) on the Instron 5565 (Universal Testing Machines, Admet, Norwood, MA) at a cross head speed of approximately 1 mm/s.

![Fig. 21. Systematic representation of 3-point bend test.](image)

Flexural strength under a load in a three-point bending test was measured by equation 4:

$$\sigma = \frac{3FL}{2bd^2}$$  \hspace{1cm} [Equation 4]

Where $F =$ load (force) at the fracture point

$L =$ length of the support span

$b =$ width of specimen

$d =$ thickness of specimen

A one way ANOVA and Tukey/Krammer tests were done to analyze the results of both fracture toughness and flexural strength. Since the mechanical properties of the prepared experimental composites are also a function of the filler dispersion in the matrix, SEM images were taken of fracture toughness samples post fracture. The images
were also taken to establish the role of the silane-bonding agent in improving fracture toughness of these composites.
7 RESULTS AND DISCUSSION

7.1 Characterization of Nanofibers

7.1.1 Scanning Electron Microscope (SEM)

First specific aim of this study was the fabrication of silica nanofibers and characterization of fabricated silica nanofiber. Quality of the SNF was characterized using SEM images. The images were used as an aid to check the presence of bead formation while electrospinning and to measure diameter of fibers before and after calcinations. SEM images (figure 22 (a,b)) showed no beading or droplet formation along the fibers spun from a 20% wt/vol concentration. Increase in concentration of solution is associated with increase in polymer entanglements which further leads to increased viscoelasticity and decrease in bead/droplet formation. Droplet formation/electrospraying can be observed when solutions of low molecular-weight polymers are used in the presence of an electrical force of sufficiently high voltage. The resulting surface tension favors the formation of beads in an effort to minimize the surface area [118]. However, increase in concentration results in increased viscoelastic forces which overcome the surface tension of the solution. Hence, 20% wt/vol concentration resulted in formation of bead-free uniform fiber morphology. The presence of smooth cylindrical fibers is likely in the event of solvent evaporating completely before reaching the collector plate. Because of production of good quality fibers using 20 wt%/vol solution, the fibers spun with 20 wt%/vol solution were considered for all experiments mentioned in this study.
Fig. 22. Represents Silica nanofibers (a, b) produced at 20 wt% precursor solution. Uniform diameter fibers were observed. No bead or droplet formation was observed.

Distribution of silica nanofiber diameter is critical to the mechanical and physical properties of the composite resin materials. Fiber specifically within a range of 150 – 500 nm are used for reinforcing in dental composites, since fibers with diameters larger than 500 nm would most likely to behave like that of a micrometer-sized fiber which results in decrease volumetric fraction and increase inter-particle spacing. On the other side, fibers with dimensions less than 150 nm in diameter will have questionable effectiveness in their ability to blunt crack growth. Therefore, fibers in ranges of diameter between the 150 – 500 nm may possess an acceptable surface area-to-volume ratio, which may also play a role in enhancing the bonding between fibers and matrix, and act as matrix toughness. Diametrical changes in SNF after calcification were observed using SEM images (figure 23 (a, b)).
Diameter of SNF before and after calcination was measured on SEM micrographs with Image Analyzer software (Image-J, Image Processing and Analysis in JAVA). Hundred counts were made per micrograph to measure and compare SNF diameter within on SEM micrograph. Figure 24 represents diametrical distribution of SNF before calcination (PVP-SNF) and after calcinations (SNF). For uncalcinated fibers (SNF-PVP), maximum percentages of fibers were observed in a range of 400-500 nm, however, for calcinated fibers (SNF-C), maximum percentages of fibers were observed in the range of 300-400 nm. On an average, the calcined Silica nanofiber (SNF-C) were about 1.4 times smaller in comparison with uncalcinated fibers (PVP-SNF), which was consistent with other studies involving the removal of a binder [92].
Efficiency of silica nanofiber production using electrospinning technique was determined in terms of the solution yields, the masses of pre- and post-calcinated samples were calculated per 4 ml of solution using equation 5.

\[
100 \times \left( \frac{M_p - M_s}{M_p} \right)
\]

[Equation 5]

Where,

MP = Mass of precursor solution

MS = Mass of calcinated solution

Efficiency of silica nanofiber production using electrospinning technique determined in terms of solution yield was approximately 7%. Although the reduction in
fiber diameter was not consistent with the mass loss after calcination, the above method of calculating mass loss is an effective way to determine the yield of the solution for scaling the process to generate larger quantities.

7.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) spectrum of SNF (uncalcinated and calcinated) was performed to confirm that calcination had occurred (Figure 25). This was done by identifying the Si–O peak at 795, 950 and 1058 cm$^{-1}$ [119]. A broad band near 3390 cm$^{-1}$ is assigned to O-H vibration. The peaks due to PVP at 1650 cm$^{-1}$ (C=O), several strong peaks methyl (-CH$_3$) 2800-3000 cm$^{-1}$ and methylene (-CH$_2$) 1400-1800 cm$^{-1}$ of ethyoxy group were present before calcination but disappear in the post-calcined sample, as expected [120].

Fig. 25. Represents FT-IR spectrum comparing calcinated and un-calcinated silica nanofibers.
7.1.3 X-Ray diffraction (XRD)

X-Ray diffraction was used to confirm the crystallographic structure of SNF and is represented in figure 26. The XRD profile of SNF showed wide peak at $2\Theta$ angle of $21^\circ$. This XRD pattern is the characteristic of amorphous silica [121].

Fig. 26. XRD of SNF with peak at $2\Theta$ angle of $21^\circ$ shows amorphous silica.
7.2 Testing of Mechanical and Physical Properties

7.2.1 Rheology (visco-elastic property)

The frequency sweep as seen in Figure 27 showed a nominal difference in viscosity with increasing shear rate and increase in filler load percentage. As discussed in section 5.4.1, rheology is an assessment of handling properties of restorative material and their ability to adapt cavity walls during restoration of cavity. Within the limitation of this study, figure 27 suggests that incorporation up to 20wt% nanofibers and 20wt% mixture of silica nanofiber and silica nanoparticle into the dental resin had minimal effect on its handling characteristics. The clear/unfilled resin and experimental groups (20wt% and 20wt%H) didn’t show significant shear thinning behavior, compared with the experimental group with high SNF filler load (35.8wt%). 35.8wt% experimental groups showed highest viscosity among all groups initially, however under constant shear rate, showed same viscosity like unfilled and groups with low filler load. This effect of experimental group 35.8wt% SNF could be because the nanofibers under constant shear tend to align along the direction of flow, thereby offering lower resistance to motion.

The highly filled composite on the other hand, displayed a Newtonian behavior with an approximately three-fold higher viscosity than the other groups. Decreased in viscosity was observed followed by gradual increase. This effect could be because of morphology of silica filler particles. Initial decrease in viscosity could be because of movement of silica filler particles away from each other under strain. However, further movement of silica filler particles were inhibited due to intermolecular attraction between filler particles which resulted in increase in viscosity with time.
Fig. 27 Represents change in viscosity of different experimental groups (20wt%, 35.8wt% and 20wt% H) compared with unfilled and highly filled (PermaFlo) composite resins.

7.2.2 Gloss

Gloss is an aspect of the visual perception of objects that is as important as color when considering the psychological impact of products on a consumer. It has been defined as 'The attribute of surfaces that causes them to have shiny or lustrous, metallic appearance’. 20wt% showed highest gloss units on the scale of 0-100, among all experimental groups, however, Tukey’s test shows no significant difference between 20wt%, 35.8wt% and PermaFlo. Unfilled resin showed lowest gloss value and 20wt% H showed higher gloss values than unfilled and lower gloss values compared to other experimental groups (figure 28).
Fig 28 Represents comparison of mean and SD gloss values of all tested groups.

7.2.3 Degree of conversion

The FT-IR spectra for uncured and cured (24 hour post cure) samples were obtained for the five resin based groups. The percentage DC and measurement of DC using FT-IR spectra for the composite groups are depicted in Figure 29 and Figure 30 respectively.

Fig. 29 Represents comparison of degree of conversion among tested groups (Mean±SD)
Degree of conversion and final properties of cured composite resins depends on polymeric matrix, percent filler particles and filler loads and percentage of photoinitiators in a composite resin system [122, 123]. The bis-GMA containing matrix possesses two aromatic rings per molecule as well as high intermolecular hydrogen bonding. This significantly reduces the mobility of the monomer chains making it highly viscous and compromising the degree of conversion. This effect can be reduced by the addition of lower molecular weight resins like TEGMA. The addition of the lower molecular weight TEGDMA improves the movement of the chains and in addition, the aliphatic nature of the molecule allows for a higher degree of conversion.

Fig. 30. Degree of conversion was measured by comparing absorption peaks of aliphatic C=C (1638 cm\(^{-1}\)) and aromatic C-C peaks (1608 cm\(^{-1}\)) using equation 5.

Since all the tested groups have same resin formulation, the degree of conversion obtained for all the groups is a function of the filler particles. The incorporation of various percentages of filler loads into resin system reduces the overall monomer content; and, hence, results in fewer aliphatic conversions of bis-GMA monomer. This is validated from the
degree of conversion seen for highly filled SNF (35.8wt%) and highly filled SFP [PermaFlo (68wt%)] composite. These results are in conjunction with similar studies involving highly filled dental composite resins [122]. No significant difference was observed between unfilled, 20wt% and 20wt% H and showed high degree of conversion in range of 62-65%. The DC values obtained for both the highly filled groups [35.8wt% and PermaFlo (68wt%)] showed lower DC than other above motioned groups. This can also be attributed to the light scattering phenomenon referred to in Section 6.2.2. Arikawa et al have shown that when light in the visible blue range is used to cure samples containing filler particles predominantly below 500 nm, there is a scattering of the light beam [124]. This scattered light results in compromised activation of photoinitiators like camphoroquinone present in the matrix, which acts as an initiator for the monomer conversion. Lower degree of conversion has also affected the performance of these samples in the analysis of wear. In order to achieve an improvement in wear mechanics of these experimental composites, the more percentage of photoinitiors must be incorporated to further increase in degree of conversion or material should be cured for longer time.

7.2.4. Polymerization Shrinkage

The results of the polymerization shrinkage tests using ACUVOL, volumetric shrinkage analyzer, confirmed that the addition of various percentages of experimental fillers loads (nanofibers and silica particles) reduced the polymerization shrinkage of the composite as represented graphically in Figure 31. The reason for this change in the polymerization dynamics of the resin is two pronged. First, the incorporation of the different nanofillers into composite resin reduces the fraction of shrinkable monomers to begin with, leading to decreased polymerization shrinkage [24]. Second, the addition of fillers greatly reduces the mobility of the monomer chains and, hence, the ability of the free radical species to react
effectively with the resin [123].

![Shrinkage (vol%)](image)

**Fig. 31.** Represents comparison of polymerization shrinkage percentages and standard deviation values of all experimental groups (Mean±SD).

The Tukey test showed a significant decrease in the percentage shrinkage values between the clear unfilled group and other tested groups. No significant difference was observed between 20wt% and 20wt% H and between 35.8wt% and Permaflo (68wt%). This data is in concurrence with the DC data, with the two tested groups (35.5wt% and PermaFlo) showing the least density of cross-linking and hence the least amount of polymerization shrinkage.

### 7.2.5. Three Body Wear

ProForm software was used to calculate volumetric loss of wear specimens. The original surfaces of the specimens were scanned using PROSCAN before they were subjected to three body wear in the Alabama Wear Testing machine. Wear facets on specimens were observed after completion of 200,000 load cycles, the specimens were re-scanned targeting the wear facets. The original and the modified (post-wear) scans were then superimposed in ProForm to create the individual volumetric wear pattern for each set of scans, as seen in Figure 32.
Fig. 32. (a,b,e,f) represents superimposed scans generated using PROFORM software in which, top surface represents pre-wear surface and bottom image represents post-wear image of all groups 20wt%, 35.8wt%, 20wt% H and Permaflo respectively. (c,d,g,f) represents wear pattern observed in all groups in same order as mentioned above.
The Alabama wear simulator translates 100,000 cycles to 1 yr of in vivo wear. The simulator uses a force of 75 N, and an impact and twisting movements. This movement helps to create a localized wear pattern which simulate wear pattern experienced in the mouth. Figure 33 provides a graphical representation of the wear volumes and standard deviations for each group. 20wt% H showed lowest volumetric loss, however, no significant difference was observed between 20wt% H and 20wt% using Tukey’s test. 35.8wt% showed highest volumetric loss whereas, PermaFlo (68wt%) showed less volumetric loss compared to 35.8wt% and higher volumetric loss as compared to 20wt% and 20wt% H.

The results show that the 5.2% SNF and the 5.2% SNP have experienced more wear compared to the traditional flowable resin group. However, the Mann-Whitney test illustrated that the variation in the volume of wear was not statistically significant for any of the four groups. It has been seen that high volume of wear can be seen in resin systems with less filler load. This is attributed to high interparticle spacing, which results in high percentage of intervening soft resin matrix in between filler particles and is worn at a much faster rate.
leading to a high early wear [116]. However, within the limitation of this study, group with high percentages of SNF (35.8wt%) and highly filled composite resin PermaFlo (68wt%) showed higher volume loss. This has been attributed to a light scattering effect occurring at a wavelength of 470 nm for nanoscaled fillers. Thus, the light intensity might have been attenuated and the degree of cure compromised, leaving behind a large amount of unreacted methacrylate groups which are mechanically weak and tend to wear easily. The FT-IR analysis of the degree of cure for these bis-GMA based composite samples can provide an insight into the wear performance of these materials.

7.2.6. Fracture Toughness and flexural strength

Fracture toughness is a property which describes the ability of a material containing crack to resist fracture and is determined based on their $K_{IC}$ values. The energy for the growth of the crack comes either from external work done or from a stored strain. The $K_{IC}$ values for all experimental groups, used in this study are shown in Figure 34.

![Fracture Toughness and flexural strength](image)

Fig. 34. Comparison of $K_{IC}$ values (with Standard deviations) for all 5 tested groups (Mean ± SD)
As expected, the addition of silanated fibers in the resin matrix improved the fracture toughness of experimental groups. One way ANOVA and Tukey tests were used to determine intergroup group differences among the fracture specimens. Addition of 20 wt% of SNF significantly increased fracture toughness. No significant difference was observed between 20 wt%, 35.8 wt% and 20 wt% H. This signifies that presence of SNF and SNF and SFP significantly stopped crack propagation. Previous studies [125] showed that increase in filler load of SNF within resin matrix results in decrease in fracture toughness due to agglomeration of fibers, however no significant decrease in fracture toughness was seen after adding SNF filler load from 20 wt% to 35.8 wt%. In order to develop a better understanding of the toughening mechanism of all the different filler types, an SEM analysis of the fractured surfaces was conducted.

The fractured specimens were examined under SEM to develop an insight into the fracture mechanics of the different compositions of the dental composite resin. The clear resin specimens showed a glassy fracture pattern as depicted in Figure 35 (a). A smooth region can be identified in Figure 35 (b), where the crack had propagated rapidly, which is also characterized by coarse and flat regions at the protruding ridges of the fractured surface. This type of brittle fracture is characterized by a sudden fracture with barely any plastic deformation [121]. Such fracture patterns are indicative of very little resistance being offered to the advancing fracture line.

The highly filled composite resin [Permaflo (68 wt%)] specimens [Figure 35 (c)] shows the appearance of cleavage faces similar to those seen in other more brittle materials like ceramics. The Permaflo contains a high percentage (68%) of silica filler particles. The micron-sized particles present in the specimens presumably redirected the fracture lines, thereby increasing the work done for fracture for this material.
Fig. 35 SEM images of fractured surfaces: (a, b) clear resin specimens with distinct ridges formed due to a brittle fracture, (c) PermaFlo specimen with areas of irregular cleavages.

The SNF reinforced composites 20wt%, 35.5 wt% and 20 wt% H, showed an improvement in fracture toughness over the clear resin. Figure 36 (a, b,c) showed a conchoidal fracture pattern with tear lines leading away from the origin of the crack. At some place, there were visible areas of polymer sheaths separating, representative of a material with low toughness. Small troughs in all figure 36 (a,b,c) were expected to be left over space after fiber pull-out under load application. This showed strong bonding between fibers and resin matrix, however at some places projected SNF can be seen from
the resin matrix. It shows that improvement is needed in silanitation of SNF. Figure 36 (c) shows non uniform distribution of SFP within the experimental groups and large agglomerates of SFP can be observed.

Fig 36 shows distribution of various filler loads and fracture pattern in 20 wt% (a), 35.8 wt% (b) and 20 wt% H (c). Arrows in a) indicates fiber pull out and SNF projected from resin matrix and crack propagation. Arrows in b) represents fracture pattern and projected SNF from resin matrix. Arrows in c) represent fiber pull-out, non uniform distribution of SFP.

The SNF reinforced samples (20wt%, 35.8wt%) showed a complex fracture pattern suggestive of a toughened matrix. As observed in Figures 30 (a, b and c) for the SNF specimens, fracture surfaces in fiber containing composites may have fibers protruding out of the matrix. This phenomenon toughens the composite, especially in case of
composites containing discontinuous fibers. A critical transfer length between fibers and matrix is necessary for effective transfer of loads. If the distance between the matrix crack and the end of discontinues fiber is less than the critical length, a fiber pull out, as seen in Figure 36 (a), occurs instead of the fiber fracturing within the matrix [116]. According to the Cottrell and Kelly model (1964), the work done against friction is stored as a pull out energy, and, subsequently creates a significant resistance to crack growth. The pulled out fibers also resulted in bridging the cracks. Hence, the fiber reinforced composites show need for an increased work to fracture. Therefore, dental composites reinforced with fibers show need for an increased work to fracture. When the distance between nanofiber end and propagating crack front is larger than the critical transfer length, fiber fracture occurs. The stress created in the interfacial region results in de-bonding of the matrix around the fiber; this frictional stress opposes the pull out of the fibers from the matrix. De-bonding of the matrix from the fibers further toughens composites since work is done in the creation of the new surfaces. However, figure 37 (a,b,c) shows smooth surfaces of trough followed by fiber pull out, which is suggestive of weak bonding between resin matrix and SNF.

In 1964, Cook-Gordon studied crack-propagation, and proposed mechanism of crack propagation. Crack always grow in a direction requiring least applied load or weakest material strength. Tensile stresses, approximately 20% the magnitude of stresses at the tip of the crack, run parallel to direction of crack propagation. Whenever a weak interface presents itself in the path of the advancing crack, de-bonding occurs ahead of the crack and a “T-shaped” blunting can be observed, thereby toughening the system. In 1974, Atkins and Marston proposed that if the fibers were oriented to create random areas of high and low shear stresses, the Cook-Gordon model would be justified.
Since, the silica fillers were surface treated with silane coupling agent before being incorporated into the matrix, the presence of a strong interfacial bonding along with improving the overall strength of the material may be expected to contribute to toughening the material. However, fracture models developed with reference to interfacial parameters have shown a strong bond to be detrimental to the fracture properties of the material [126]. A weaker interfacial bond on the other hand, is preferred in preventing crack propagation since fiber pull out and higher stresses are created in the interfacial matrix. Since the SNF reinforced specimens performed well under fracture, this suggests the presence of areas of both strong and weak bonding existing within the SNF reinforced matrix [127]. The randomly dispersed fibers with no distinct orientation may presumably have contributed to this discrepancy in interfacial bonding.
8. NULL HYPOTHESIS REJECTION

No difference will be observed in the mechanical and physical properties of flowable composites produced by adding different filler load, compared with unfilled composite resin and highly filled flowable composite resin was rejected.
The objective of this study was to fabricate silica nanofibers and blend them with commercially available resin monomer to form highly reinforced direct filling flowable composite resin with improved mechanical and physical properties. The SNF were fabricated using electrospinning technique, which was optimized to obtain bead free morphology cylindrical fibers with average diameters in the range of 300 - 450 nm. The electrospun SNF heat treated in order to remove the binder polymer. Characterization of morphology of prepared fibers was done using scanning electron microscopy (SEM), for any surface defects, FT-IR was used to determine composition of the fibers and crystallography of SNF was determined using XRD. The silica fibers were then surface treated at ULTRADENT, Inc., Utah, with silane coupling agent in order to improve the bonding between the fibers and the bis-GMA/TEGDMA resin mixture into which they were to be incorporated. Experimental groups with various wt% of filler loads were prepared (20wt%, 35.8wt% and 20wt% H). Unfilled and highly filled [PermaFlo (68wt%)] were tested as negative and positive control respectively. The samples containing the SNF were translucent to light, and were glossy after polishing. Since esthetics is an important criterion for composite restorations, these materials hold promise in the cosmetic restoration segment. The improvement in all mechanical properties were observed after incorporation of SNF and SNF:SFP mixture. Among all the experimental groups 20wt% H showed highest fracture toughness, flexural strength and wear resistant. Incorporation of SNF also improved
rheological properties of flowable composite. 35.8wt% experimental group showed best handling properties under shear rate and 20wt% showed highest gloss values. 20wt% H showed highest degree of conversion whereas 35.8wt% showed lowest degree of conversion. All experimental groups showed high polymerization shrinkage as compared to PermaFlo.

The SNF have also shown the ability to be silanated and dispersed evenly into the resin matrix, thereby negating the ill effects of filler agglomeration associated with nano-dimension particles. By increasing the filler loading and filler distribution, better control of the inter-particulate spacing in the prepared composites can be achieved and the wear resistance of these materials may be improved. However, due to the limitations of this study, further work could not be accomplished.

Future research in this area should be directed towards the development of multiscaled composites containing various percentages of hybrid fillers, micronsized particulate fillers along with the silica nanofibers, optimizing the length of SNF and improvement of coupling agent application is required. Understanding the effect of the interaction of all these fillers on the properties of dental composite provides a stimulating research opportunity. The new generation of dental composites with the combination of fillers proposed, will have enhanced clinical performance.
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