Effect of TEOS Electrospun Nanofiber Modified Resin on Interlaminar Shear Strength of Glass Fiber/Epoxy Composite

Dattaji K. Shinde, Ajit D. Kelkar

Abstract—Interlaminar shear strength (ILSS) of fiber reinforced polymer composite is an important property for most of the structural applications. Matrix modification is an effective method used to improve the interlaminar shear strength of composite. In this paper, EPON 862/w epoxy system was modified using Tetraethyl orthosilicate (TEOS) electrospun nanofibers (ENFs) which were produced using electrospinning method. Unmodified and nanofibers modified resins were used to fabricate glass fiber reinforced polymer composite (GFRP) using H-VARTM method. The ILSS of the Glass Fiber Reinforced Polymeric Composites (GFRP) was investigated. The study shows that introduction of TEOS ENFs in the epoxy resin enhanced the ILSS of GFRPby 15% with 0.6% wt. fraction of TEOS ENFs.

Keywords—Electrospun nanofibers, H-VARTM, Interlaminar shear strength (ILSS), Matrix modification.

I. INTRODUCTION

IN the last decades use of a glass fiber reinforced polymer composite (GFRP) for structural applications including aerospace, defense, automobile and recreational has increased exponentially due to their high mechanical strength to weight ratios [1]. Typically to improve the ILSS conventional methods such as stitching, z pining, 3D braiding and adhesive interleaf are used [2]-[3]. Interlaminar shear strength (ILSS) of fiber reinforced composites becomes a limiting design characteristic for structural applications. However, these composites have some limitations related to matrix dominated properties which will further limit their extensive use in various applications [4]. Polymer matrix properties can be improved by introducing small amounts of organic or inorganic nanofillers as secondary reinforcements in the matrix. Several methods have been used to incorporate nanoparticles such as single and multi-walled carbon nanotubes (SWCNTs and MWCNTs), nanoclays and carbon nanofibers (CNFs) to improve the matrix properties in composite materials [5]-[8].

Conventional manufacturing processes of GFRP do not help to make reinforcing fibers in the thickness direction strong enough to carry a large transverse loading [9]. If nanoparticles

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are arranged along thickness direction, that will enhance the ILSS by transferring load from matrix to fiber. Using VARTM process with distribution media are assisted has an advantage to orient nanoparticles into the thickness direction [10]. As the distribution media has higher permeability than fiber layers and nanoparticles can easily move in the thickness direction through a distribution media rather than flowing across fiber layers. A prerequisite to improve the properties of nanocomposites requires an excellent dispersion of nanomaterials in the matrix. Carbon nanofiber (CNF) loaded GFRPC showed higher ILSS due to better interfacial bonding between the fiber and matrix due to the presence of CNFs [11]. The addition of 0.5 wt. % MWCNTs and 10 phr n-butylglycidyl ether (BGE) leads to the 25.4% increase in the ILSS for the glass fiber reinforced composite [12]. The use of electrospun TEOS nanofibers interleaved layers in the S-2 glass fiber composite has shown 21% improvement in the interlaminar shear strength impacting the delamination characteristic of the composite and their usefulness for structural application [13]. At present, there is no standard method which can mix nanoparticles and resin however, several dispersion methods are attempted by many researchers.

The literature review indicated that very little work has been reported on the role of matrix modification by combining TEOS electrospun nanofibers (ENFs) and EPON 862 resin on the ILSS of GFRP composites. In this paper, TEOS ENFs are mixed homogeneously in the epoxy resin and then curing agent W was added. Unmodified and nanofiber modified epoxy resins were then used to fabricate glass fiber reinforced epoxy composites using H-VARTM method. The ILSS of the glass fiber reinforced composites were investigated as a function of the matrix modification. The fracture surfaces of the fiber composites are examined by scanning electron microscopy (SEM) and the micrographs are used to explain the results for the ILSS.

II. EXPERIMENTAL

A. Materials

Plain weave woven S-glass fibers (GFs) BGF 240 (S-2 463-AA-250) were purchased from BGF industries Inc. Greensboro, NC, USA. The epoxy resin used in this work was phenol formaldehyde polymer glycidyl ether called EPON Resin 862 and the curing agent was diethylmethylbenzediamnine EPIKURE W both were

purchased from Miller Stephenson Chemical Co. Inc., Danbury, CT USA. The precursor tetraethyl orthosilicate (TEOS) for electrospun nanofibers was purchased from Across Organic New Jersey USA was used to modify the epoxy matrix.

1. Electrospinning of TEOS Nanofibers

Electrospinning is one of the major approaches for developing continuous nano-scale fibers with diameters ranging from tens to hundreds of nanometers. The basic electrospinning process used in this study is an adaptation of electrostatic spinning method introduced by Formhals in 1934 [14]. A comprehensive analysis of electrospinning setup and processing is available in the literature [15]. Tetraethyl Orthosilate (TEOS) used as sol-gel, electrospinning utilizes electrical force instead of mechanical force to drive the spinning process and produce nanofibers having diameters at least one or two order of magnitude smaller. Before using the TEOS ENFs in composites, were sintered at 600°C for six hours. After sintering, there was about 30–50% reduction in the diameter of nanofibers. This reduction in diameter lends to more surface area and improvement in permeability of random nanofibers mats which in turn improve performance of the nanofibers in composites [16]. The schematic diagram of a single-needle electrospinning setup is shown Fig. 1.
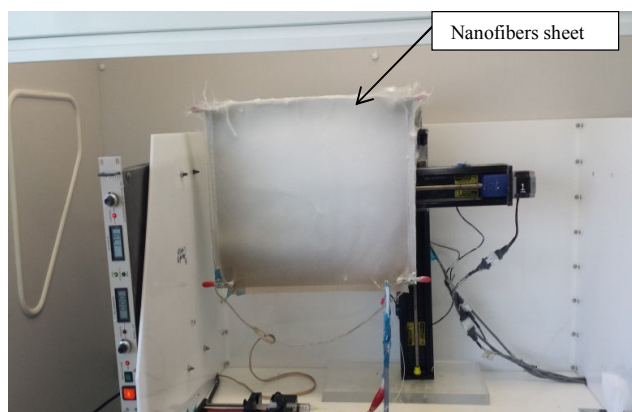

Fig. 1 Electrospinning setup

The TEOS sol-gel solution was used for electrospinning on the flat plate collector with Teflon sheet [13] as shown in Fig. 1. These electrospun TEOSnanofibers were sintered at 600°C for 6 hours to reduce the diameter and to evaporate ethanol from the nanofibers. Before, sintering diameter of nanofibers was in the range of 300-500nm and are shown in Fig. 2. After the sintering the diameter of nanofibers were reduced and found in the range of 250-300nm and are shown in Fig. 3.
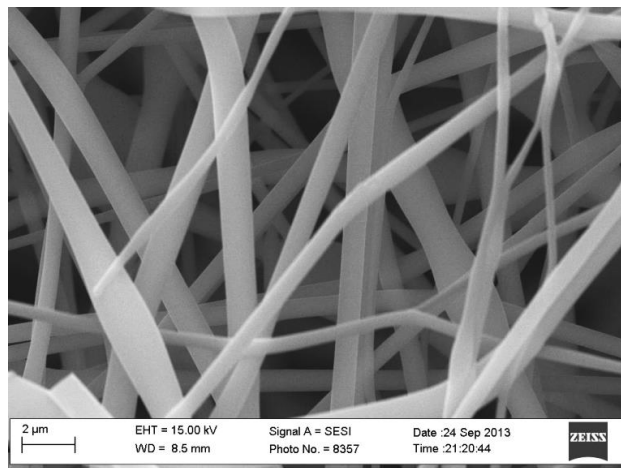

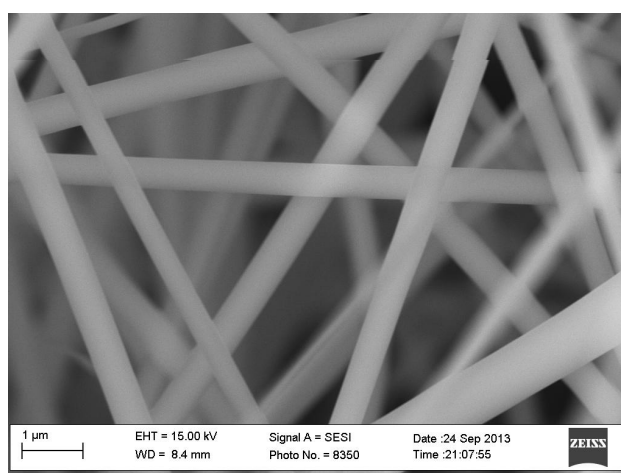Fig. 2 SEM image of TEOS electrospun nanofibers before sintering

Fig. 3 SEM image of TEOS electrospun nanofibers after sintering

B. Fabrication of Composite Panel

Five composite panels of size 305mm x 204mm were fabricated using H-VARTM method as shown in Fig. 5. First composite panel was fabricated with 4 plies of plain weave woven S-2 glass fibers and EPON resin. The resin and curing agent were mixed in 100:26.4 ratio. Rests of the panels were fabricated by using 0.2, 0.4, 0.6, and 0.8 wt.% of TEOS ENFs which were used to modify the resin. In the first step four weights of TEOS ENFs were measured as 0.2, 0.4, 0.6, and 0.8% of the weight of the resin. In the second step composites panel were fabricated using 400g epoxy resin mixed with TEOS ENFs chopped fibers by manually stirring for 5 minutes and then sonicating using Sonics Vibra-cell with 32% amplitude for 1 hour. Schematic diagram of sonication process is shown in Fig. 4. After the sonication curing agent W of weight 104g were added to epoxy in resin mixed with electrospun nanofibers. All five resin mixtures with W then were degasified for 20 minutes at 80°C in the close oven set up. All five mixtures of resin were then infused in 4 plies of S-2 glass plain weave fiber glass using H-VARTM method as shown in Fig. 5.
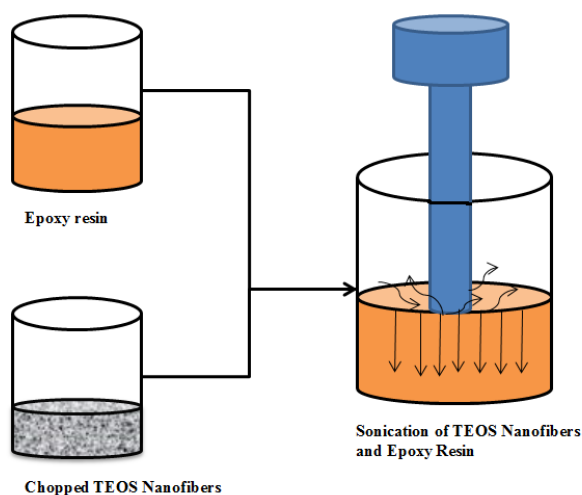
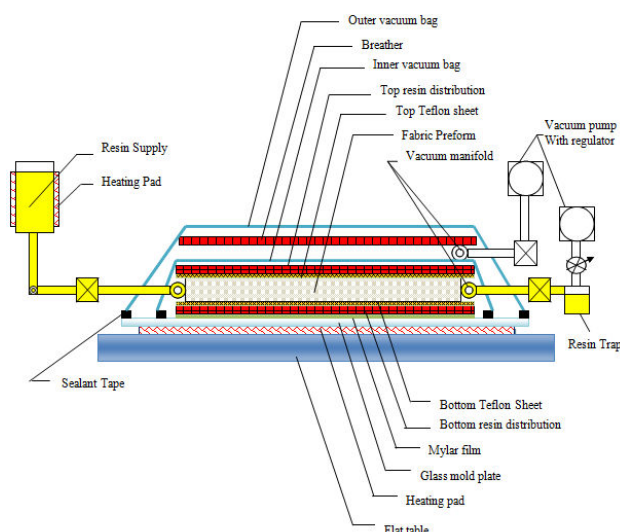Fig. 4 Schematic drawing of sonication for mixing of TEOS ENFs and Epoxy resin

Fig. 5 H -VARTM process setup [13]

Resin mixture infused laminated plies were cured with a curing cycle operated at 250 ^{0} F for 2 hours. After curing the composite panels were visually checked for visible voids and surface defects. It was observed that viscosity of resin mixed with 0.8 wt. % of TEOS ENFs was considerably more and took longer time to flow as compared with rest of the four composite panels. The composite panels were cut into five specimen of size 41mm x 6.3mm as per the ASTM D2344 standard using water jet cutting machine.

C. Mechanical Characterization

The fiber volume fraction ratios was calculated using matrix burn test as per ASTM D3171-99 Standard for unmodified and modified resin matrix composite. The volume fraction ratios was 57.96%.The short beam shear (three-point bending) test was conducted on an INSTRON 3384 universal testing machine using 5 kN load cell with a crosshead speed of 1.27 mm/min. The span-to-thickness ratio in the short beam shear test was 6. The test was conducted as per the ASTM D2344; the apparent inter laminar shear strength (ILSS)τ was calculated from the classical beam by using (1).

$$\tau = \frac{3P}{4bh} \qquad (1)$$

where τ is the maximum interlaminar shear strength at failure, P is the maximum load, b is the specimen width and h is the specimen thickness. In this testing more than five samples were tested in each case. Unmodified and modified resin matrices were examined using SEM. In addition the failed samples fracture surfaces from short beam shear test, were examined using SEM.

III. RESULT AND DISCUSSION

A. Interlaminar Shear Strength (ILSS)

Five different types of composites coupons were fabricated for unmodified and modified epoxy matrices. Specimen was marked for unmodified epoxy/glass fiber composite-GF and modified matrix with 0.2, 0.4, 0.6, and 0.8wt. % of sintered TEOS ENFs epoxy/glass fiber composite and were labeled as 1NF, 2NF, 3NF, and 4NF respectively. Composite structures in the service cycle might encounter high stresses which lead in crack propagation through fiber matrix interfaces. Hence, stronger adhesion between fiber and matrix, higher strength, and higher toughened matrix are desired in composite material design. Modified Short beam shear (MSBS) tests were performed on conventional and nanophased GFRP to measure their interlaminar shear strengths. In conventional ILSS test interlaminar shear failure may not occur at the mid plane and it is difficult to assure pure shear failure [19]. In MSBS test, failure occurs due to a combination of fiber rupture, micro-buckling, indentation, flexure, and interlaminar shear cracking of the specimens [6], [20]. ILSS test results are presented in Fig. 8. Higher ILSS was observed in 0.6wt. % of TEOS ENFs modified epoxy/glass fiber compared to conventional composites probably due to the initiation of crack arrest mechanisms in front of nanofibers embedded in epoxy.

The short beam shear method was then used to measure interlaminar shear strength of fiber glass reinforced composites [4]. The short beam shear tests were performed on the different nanofiber modified matrix and the results are shown in Fig. 6. Fig. 6 shows that all load–displacement curves rise gradually and drop suddenly. The modified matrix with 0.6 wt. % of TEOS ENFs shows highest load of 834 N and then suddenly dropped. Also 0.2 wt. % of TEOS ENFs in modified matrix has shown lowest load and was 627N. The enhancements in interlaminar shear strength of glass fiber reinforced composites with and without matrix modification of epoxy matrix is shown in Table I.
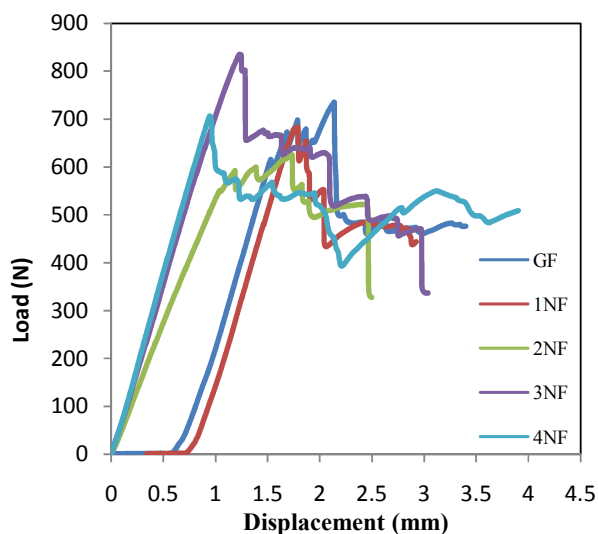
Fig. 6 Short beam shear test load versus displacement curves of glass fiber reinforced composites based on unmodified epoxy GF, modified epoxy with 1NF, 2NF, 3NF, and 4NF (0.2, 0.4 , 0.6 and 0.8 wt. %.)

TABLE I
ENHANCEMENTS IN INTERLAMINAR SHEAR STRENGTH OF GLASS FIBER REINFORCED COMPOSITES BY MODIFICATION OF EPOXY MATRIX

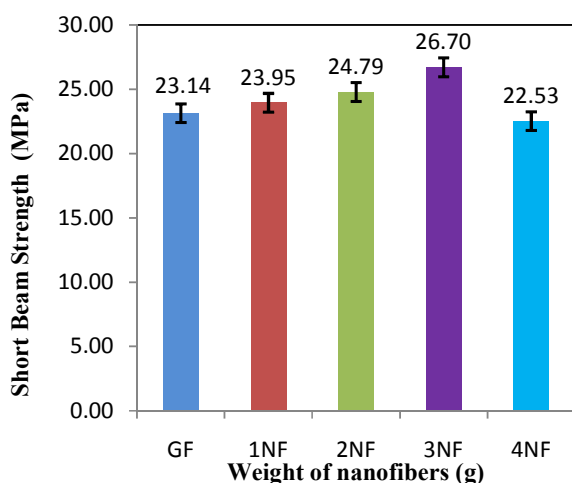| Matrix types	Weight % of TEOS ENF	ILSS (MPa)	Enhancement (%)
Epoxy (GF)	0	23.14	0
1NF and Epoxy	0.2	23.95	3.51
2NF and Epoxy	0.4	24.79	7.12
3NF and Epoxy	0.6	26.70	15.41
4NF and Epoxy	0.8	22.53	-2.65

Fig. 7 Interlaminar shear strength of glass fiber reinforced composites with unmodified epoxy GF, modified epoxy with 1NF, 2NF, 3NF, and 4NF (0.2, 0.4 , 0.6 and 0.8 wt. %.)

The interlaminar shear strengths obtained in the three point bending test are shown in Fig. 7 and shows that the ILSS of the modified epoxy/glass fiber composite is higher than that of the unmodified epoxy/glass fiber composite except for 0.8 wt.

% of TEOS ENFs modified resin. For the 0.2wt. % of TEOS ENFs ILSS improved by about 4%. For 0.4wt. % of TEOS ENFs resulted into improvement of 7% in ILSS of glass fiber composite, and for 0.6 wt. % of TEOS ENFs ILSS improved by 15%.

However it was interesting to observe that addition of 0.8 wt. % of TEOS ENFs did not show any improvement in ILSS of glass fiber composite but in this particular case the addition of TEOS nanofibers resulted into significant decrease in ILSS of the composite. This may be because of more viscosity of the resin mixture, which might have resulted into the resistance to flow in the glass fiber plies laminates and less impregnation of the glass fiber during infusion of resin during H-VARTM process. The ILSS of the fiber glass composite depends on the epoxy matrix modification [17]-[18]. Modification of epoxy matrix by 0.6 wt. % of TEOS ENFs might lead to an improved interfacial adhesion between glass fiber and epoxy matrix are shown in Fig. 8. The strong interfacial bond between fiber glass and TEOS ENFs modified epoxy would lead to increase in the ILSS. The ILSS of the glass fiber reinforced composite showed about 15% improvement in the ILSS.

B. Fracture Analysis

Fracture analysis of modified short beam shear test samples of glass fiber/epoxy composite with unmodified and modified epoxy matrix was studied using fracture morphology of the failed specimens and dispersion of TEOS ENGs in epoxy resin using SEM Zeiss model EVOLS10 machine and is shown in Figs. 8 and 9. The interlaminar shear failure resulted due to delamination which typically occurred at the central plane of the specimen. It was observed that an unmodified epoxy resin glass fiber composite surface was smooth and failure occurred due to single delamination at the mid planeplies of the laminate. In case of TEOS ENFs modified epoxy resin composites, delamination was not smooth and occurs at more than one plane. When a bending load was applied to the composite structures, first cracks were generated in the matrix and stress is then transferred from lower modulus matrix to the TEOS ENFs and then to the long fiber by bridging effect in the interfacial region. In this case, TEOS ENFs acted as coupling between the glass fibers and epoxy resin [11]. For better understanding of the fracture morphology of the samples were investigated using higher magnification SEM micrographs.

The SEM micrograph of crack occurred and the fractured surfaces of the unmodified resin matrix glass fiber composite are shown in Figs. 8 (a) and (b). The surface of the fiber was clean, and very less matrix adhered to the fiber. This indicates that the bonding between the fiber and matrix was weak. The fracture surface in modified epoxy resin with TEOS ENFs is shown in Figs. 8 (c) and (d) that indicate that the crack was not generated between the ply laminates and epoxy resin is adhering to the glass fiber and has strong interfacial adhesion than the unmodified epoxy resin [18]. Tin the situation when the resin was well bonded to the fiber surface which provided increase in significant plastic deformation and that enhanced

the mechanical properties of the composite. The rough surface areas are shown in the Figs. 9 (d), (f), and (h), for modified epoxy glass fiber composite, which shows the surfaces were rougher than the unmodified epoxy resin glass fiber composite. This shows stronger bonding at the interface and higher frication coefficient in the ILSS tests. More is the rougher surface that acts as mechanical interlocking system which contributes to higher ILSS.

Fig. 9 SEM images for dispersion of TEOS electrospun nanofibers in epoxy resin (a) 15.45 KX, and (b) 34.91 KX
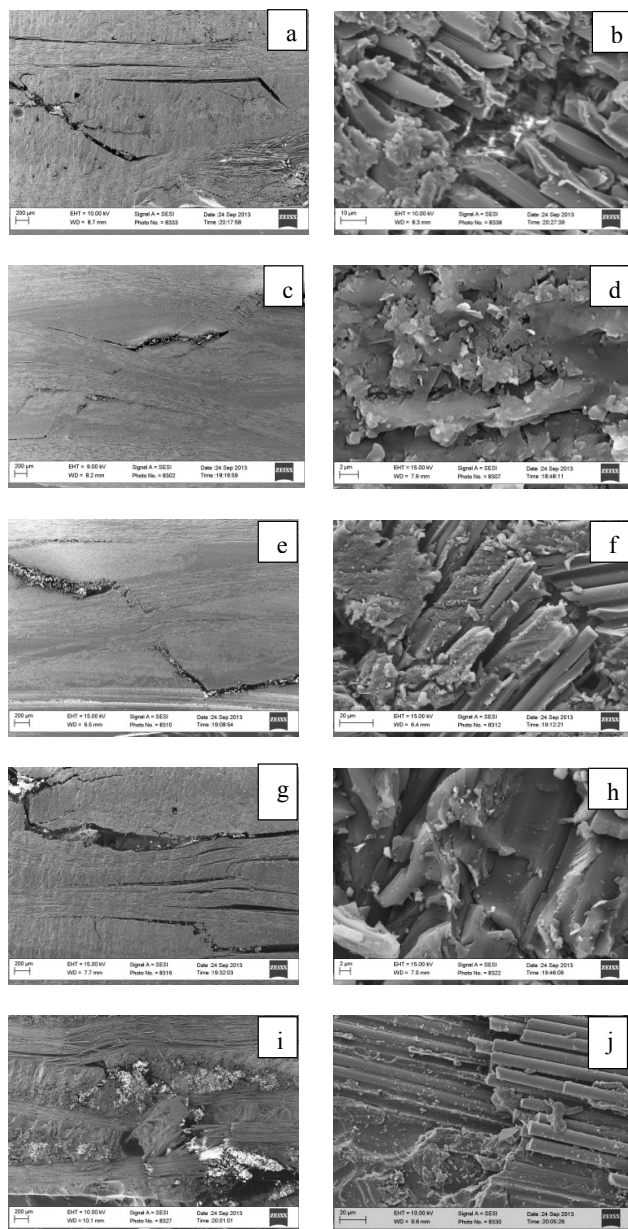
Fig. 8 SEM images for specimens of glass fiber reinforced composite after three point bending test and their fracture surfaces based on (a) and (b) unmodified epoxy, (c) and (d) 0.2% wt. TEOS ENFs modified epoxy, (e) and (f) 0.4% wt. TEOS ENFs modified epoxy, (g) and (h) 0.6% wt. TEOS ENFs modified epoxy, (i) and (j) 0.8% wt. TEOS ENFs modified epoxy
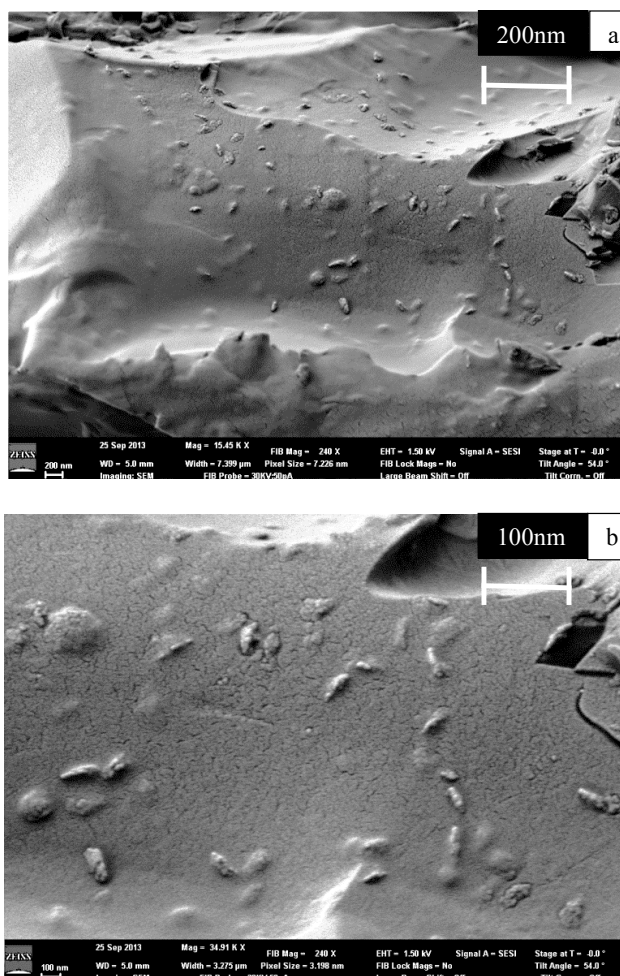
Especially, the rough fracture surfaces indicated that TEOS ENFs employed toughened epoxy/glass fiber reinforced composites require more energy to delaminate. This may be the main reason that leads to increase in ILSS of glass fiber composite based on modified epoxy with 0.2, 0.4, and 0.6 % wt. of TEOS ENFs. However, with 0.8%wt. of TEOS ENFs have shown decrease in ILSS. Figs. 8 (i) and (j) show smooth fracture surface and more TEOS ENFs were agglomerated in the matrix. Figs. 9 (a) and (b) show SEM images for dispersion and agglomeration of TEOS ENFs in the epoxy resin. These ENFs were agglomerated because of the higher attractive van der Waals forces, which reduces the strength of the nanocomposite by stress concentration effect [11]. Agglomerates of TEOS ENFS, called nanoropes, are difficult to separate and infiltrate with matrix are clearly shown in Fig. 9 (b). This agglomeration of TEOS ENFs leads to less impregnation glass fibers in modified epoxy resin with 0.8% wt. of TEOS ENFs. The time taken to flow the modified resin was higher than rest of glass fiber composite panels because of more viscosity modified epoxy resin. There may be some dry

fibers in the composite due to agglomeration of TEOS ENFs in the epoxy matrix.

IV. CONCLUSIONS

The effect of modification of matrix by using TEOS electrospun nanofibers (ENFs) on interlaminar shear strength of plain weave woven glass fiber reinforced epoxy composites was investigated. The modification of epoxy matrix by introduction of TEOS ENFs resulted into enhanced interlaminar shear strength of glass fiber composites. Best dispersion of TEOS ENFs was observed for the range of 0.2% to 0.8% wt. of TEOS ENFs in the epoxy resin. The proper resin flow was observed except when 0.8% wt. of TEOS ENFs was mixed in the resin. With introducing up to 0.6 %wt. of TEOS ENFs in the epoxy resin have shown up to 15% increase in the interlaminar shear strength compared to unmodified case. Micrograph examinations showed that the introduction of TEOS ENFs resulted in enhanced glass fiber/epoxy interfacial adhesion by interlocking and the stress transfer capability of TEOS ENFs in the interfacial region of the fiber and matrix. This might be the main reason for the enhancement in the interlaminar shear strength of glass fiber reinforced composites with modification of epoxy matrix using TEOS ENFs. Further increase in percentage weight of TEOS ENFs for modification of epoxy resin has shown decrease in interlaminar strength, this may be due to less impregnation of glass fiber, more viscosity of modified epoxy resin and increase in the agglomeration of TEOS ENFs due to higher attractive van der Waals forces.

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Dr. Ajit D. Kelkar is a Professor and Chair of Nanoengineering department at Joint School of Nanoscience and Nanoengineering. He also serves as an Associate Director for the Center for Advanced Materials and Smart Structures. For the past twenty five years he has been working in the area of performance evaluation and modeling of polymeric composites and ceramic matrix composites. He has worked with several federal laboratories in the area of fatigue, impact and finite element modeling of woven composites including US Army, US Air force, NASA-Langley Research Center, National science Foundation, Office of Naval Research, and Oak Ridge National Laboratory. In addition he has collaborated with Rice University, Texas A&M University, Tuskegee University, Air Force Institute of Technology, University of Dayton, Florida State University, Prairie View A&M University, University of Delaware, Texas State University, University of Minnesota, University of California, and San Diego. His expertise are in the area of low cost fabrication and processing of woven composites using VARTM process, fatigue and impact testing of composites, analytical modeling of woven composites. Presently he is involved in the development of nano engineered multifunctional materials using XD CNTs and electro spun fiber materials. He

is also involved in reengineering of several H-46 and H-47 helicopter components for NAVAIR using out of autoclave processing. In the past he has worked on the one step processing of Composite Armored Vehicle using low cost VARTM method in consortium with University of Delaware-CCM and UC San Diego. In the modeling area he is working on blast simulations for the Humvee vehicles subjected to various TNT blasts loadings and atomistic modeling of polymers embedded with CNTs and alumina nanoparticles. He is also involved in high velocity impact modeling of ceramic matrix composites and polymeric matrix composites embedded with electrospun nanofibers. He has published over two hundred papers in these areas. In addition he has edited a book in the area of Nano Engineered materials. He is member of several professional societies including ASME, SAMPE, AIAA, ASM, and ASEE.