An Investigation on Microstructure and Physical Parameters of Nano-enhanced Polymer Composites with Fiber Reinforcements

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Abstract

Polymer based Nanocomposites have been emerging as extremely convincing materials owing to their improved electrical, mechanical, thermal and corrosion characteristics. In the present research, fabrication of Natural fiber composites infused with nanoparticles and without nanoparticles have been carried out using hand lay-up technique. It has been observed through comparative analysis of physical properties and surface morphology that composites reinforced with Nano-silica exhibit better surface properties and strength.

The tensile and compressive strengths of the two composites were measured using ASTM 3039 and it revealed that the addition of fumed silica as nanoparticles increased the tensile strength of the specimen to 7.14 kPa/ N as compared to the tensile strength of 5.92 kPa/N of the specimen without nanoparticles. The compressive displacement at break also increased from 2.07 mm for the specimen without nanofiller to 3.35 mm for the specimen with nanofiller.

Microscopic analysis (FESEM) was also performed on both the specimens of composites. The microstructure of hybrid natural fibres reinforced composites without nanofillers show cracks, voids and fiber breakage whilst composites with nanofillers exhibited a homogeneous and uniform distribution of nano-scaled fumed silica in the epoxy matrix with decreased void content and thereby increasing the interfacial strength of the composite.

Keywords-

Nanocomposites, Mechanical properties, Surface properties, Microstructural analysis, Lay-up method

1. Introduction

Nanocomposites have been proposed as an advancement over traditional composites and have successfully found applications in various economic sectors, including construction, packaging, biomedical, cosmetics, aerospace, and the automotive industry. To maximize the potential of these hybrid natural fiber composites, it is crucial to investigate the properties of the selected fibres and matrix. The primary challenge encountered in the fabrication of these composites lies in achieving strong adhesion between the fibres and the matrix.

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To address this challenge and improve compatibility, various physical, chemical, and biological methods have been employed. According to Ravi, M. et al. [1], physical treatments involve techniques such as plasma treatment, where the surface is prepared to establish stable covalent bonds.

Chemical treatments are used to increase the surface roughness of the fibres. Surface modification of natural fibres improves the compatibility with hydrophobic polymers. Chemical treatments such as using appropriate compatibilizers improve the bonding between the surface of the fibres and the polymer matrix. Researchers have carried out various surface modification techniques such as oxidation processes, silane treatment of the fibres, benzoylation, acetylation, monomers grafting and modification using various coupling agents such as silicon, titanium and zirconium. Alkaline treatment is employed for reinforcing natural fibres with thermoplastics and thermosets. Acrylation is another chemical treatment of cellulosic fibres.

Biological treatments include retting process where microorganisms such as bacteria and fungi are used. These traditional methods of surface modification improve the compatibility but requires multiple processing steps.

The incorporation of nanoparticles presents significant advantages over traditional methods in various sectors, including energy storage, biotechnology, cosmetics, packaging, communication, and security. The fabrication of nanocomposites, which involves integrating nanofillers as reinforcements in the fiber or matrix, along with advanced nano-enabled processing techniques, has emerged as a superior approach in the field of material science.

The utilization of nanoparticles as reinforcing fillers in composites enhances their efficiency by fostering improved interfacial bonding with the polymer matrix. Researchers have explored the integration of nanoparticles into natural fiber-reinforced composites to impart specific properties such as antibacterial attributes, resistance to odors, hydrophobic characteristics, and UV protection.

Amjad Adnan et.al.[2] studied the effect of concentration of Alumina and Magnesia nanoparticles in the jute and flax composites fabricated using vacuum bagging method and studies revealed that as the concentration of nanofillers were increased, the void content in the composites decreased.

Han Yanting et.al.[3] carried out investigations on fumed silica based nonionic waterborne polyurethane nanocomposites and observed superior hydrophobicity, thermal insulation as well as UV irradiation.

In a study by Wu Yingi et al. [4], nanofillers of ZnO nanoparticles were incorporated into Natural Fiber Reinforced Biocomposites (NFRBC) using vacuum-assisted resin transfer molding. When compared to glass fiber sheet molding compound (GF SMC), the NFRBC exhibited enhanced mechanical strength and improved water resistance. Life cycle assessments indicated that these nanocomposites are environmentally friendly and have the potential to replace GF SMCs.

In a research effort led by EA Franco Urquiza et al. [5], kenaf fiber reinforced epoxy resin was examined with the addition of various nanoparticles, including carbon, layered silicates,

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and metal oxides. The study revealed that graphene and layered silicates imparted greater strength to the fibres compared to metal oxide nanoparticles.

GL Devnani et al. [6] conducted a comprehensive review on different types of nanofillers and their effects on the properties of natural fiber composites. Several studies highlighted that the introduction of nanoclay reduced water absorption capacity. Additionally, nano silica and carbon nanotubes were found to enhance the mechanical properties of various fiber and polymer composites. Coating flax fibres with Nano TiO2 using the dip coating method was observed to improve mechanical strength, water absorption characteristics, and interlaminar fracture toughness.

Abebayehu et al. [7] undertook the fabrication of biocomposite materials by reinforcing sisal fibres with waste polypropylene at varying fiber loading ratios. The composites' surface was rendered superhydrophobic through treatment with chromic acid and stearic acid.

In the work by T. Raja et al. [8], the focus was on fabricating banyan fiber-reinforced epoxy composites with sawdust nanofillers. Five samples were prepared with different weight ratios, maintaining a matrix of 60% and varying the percentage of fiber and filler at 40%. The study compared the flexural, tensile, and impact strengths, as well as the hardness of each hybrid sample. Surface interaction and failure mode of the laminates were investigated through SEM analysis.

Juliana Cruz et al. [9] highlighted that addressing the limitations of natural fibres, such as moisture absorption, low thermal or chemical resistance, and weak interfacial adhesion with polymeric matrices, can be achieved by modifying the surface of natural fibres. This modification enhances their suitability for various applications.

Tarrio Savedra et al. [10] conducted a study on the thermal stability and thermal degradation of fumed silica-infused epoxy composites, analyzed through TGA curve analysis.

Manaudis P. et.al. [11] studied Coatings of silica nanoparticles have proved to be effective in protecting stone – based monuments by increasing the surface roughness and which renders the surface water repellent. PMMA and PFPE polymers were used to form nanocomposite films which were successful in making the surfaces hydrophobic.

Bingbing Xu et.al.[12] carried out the research work in which hexadecyltrimethoxysilane HDTMS modified nano SiO2. Through water contact angle measurements, FTIR, Thermogravimetric Analysis, SEM analysis, it was observed that nano Silica showed superhydrophobicity.

In the research conducted by Duermae et al. [13], an examination of the thermal and mechanical properties of polybenzoxine composites filled with nano silica particles revealed that at a 30% weight concentration of nanoparticles, the composites displayed minimal voids.

Sunil Manohar Maharana et al. [14] delved into the impact of chemical treatment and fumed silica coating on the tensile and thermogravimetric properties of jute yarn. The study observed a significant increase in both ultimate tensile load and thermal stability for fibres coated with fumed silica.

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Tej Singh et al. [15] explored the influence of nanosilica on the mechanical and wear properties of natural fiber composites. These composites, prepared with hemp-sisal reinforcements and nanosilica, demonstrated variations in proportions of nanoparticles from 0% to 4%. The addition of nanoparticles led to an increase in the density of the composites, accompanied by a decrease in void content.

Jinpeng Feng et.al.[16] reported in their paper that composites prepared with micro/nano fumed silica possessed good thermal insulating properties with a very low value of thermal conductivity.

This paper discusses the fabrication of natural fibre composites reinforced with fumed nano-silica particles. These composites are also compared with the non-reinforced ones in terms of their physical and structural properties. This research is an effort to visibly ensure that these properties may be significantly altered on incorporation of nanoparticles in the natural fiber composites. This positive alteration in the properties may be utilized in various applications and is a way forward in the design of stronger components for household and industrial utilization.

2. Materials and Experimental Methodology

1) **Natural Fibres Selection-** Amongst the various natural fibres such as plant fibres, animal fibres and mineral fibres, plant fibres have been selected for this experimental work as they are rich in cellulose content. Date Palm fiber, Sugarcane bagasse and Groundnut shells are used for this research as these fibres are abundantly available in the local regions and moreover, they have high stiffness and strength, easily degradable, better thermal and insulation properties than synthetic fibres.

2) **Matrix Selection-** Thermosetting polymers which forms branched 3D chain like structures such as epoxy, phenolics, silicone etc. are permanent setting polymers which usually sets and gets hardened after the molding process are used as the matrix for fabricating the composites. In this investigation, Epoxy LY556 and Hardener HY951 in the ratio of 10:1 respectively is used as the matrix material.

3) **Selection of Nanoparticles-** Nanoparticles are extremely fine particles in the range of 1-100nm.Nanoparticles are usually spherical in shape and have high surface area to volume ratio. Nanoparticles are of various types such as carbon based, metal, ceramic, semiconductor, polymeric nanoparticles. For the composite preparation, fumed silica has been used as nanoparticles in this experiment.

2.1 Characteristics of Fumed Silica

Pyrogenic silica or silicon dioxide commonly known as Fumed Silica is a white powder with low bulk density and acts as a strong thickening agent. It is considered as a nanoparticle with particle size in the range of 5-50nm. These nanoparticles are non- porous and very light and fluffy.

Aggregates of fumed silica are found to have linear, branched, ellipsoidal or spheroidal shapes. Nanosilica powder when mixed with epoxy resin or polyester resin forms a very

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smooth and filleting compound which is strong and resistant to abrasions. It enhances mechanical properties, increases cohesiveness and reduces permeability.

The advantage of fumed silica being used as nanofillers is that it has high specific surface area, its industrial synthesis is convenient and has wide commercial availability.µ

3. Fabrication Methodology

In the composite fabrication process, three natural fibres, namely Date Palm fiber (70%), Sugarcane Bagasse (15%), and Groundnut shell (15%), were chosen. These fibres underwent a thorough washing and a 12-hour soaking period in distilled water to eliminate dust and impurities. Subsequently, the fibres were air-dried at room temperature. To enhance the composite's strength, Sugarcane Bagasse and groundnut shell were ground into particulate form.

The fabrication utilized the hand lay-up technique for developing Fumed silica-reinforced hybrid nano-composites. The selected fibres were arranged in the mold, and a mixture of thermoset epoxy (LY 556) and curing agent hardener (HY 951) in a 10:1 ratio (epoxy to hardener) was gently poured over the fibres. A roller was then used to compress the fibres, epoxy, and hardener, and through vacuum bagging, air voids were effectively removed from the composite. **Fig-1** shows the various raw materials used for fabrication of the specimen i.e. the natural fibres namely Date Palm, Sugarcane Bagasse and groundnut shell fibres, nanoparticles of fumed silica and Epoxy LY556 and hardener HY951.

Two specimens of hybrid composites are prepared – Specimen A without adding nanofiller and Specimen B with the addition of nanofiller of fumed silica. The fabricated specimen 1 has 10% weight of the fibres and 90% weight of the matrix and specimen 2 has 9.5% weight of the fiber, 0.5% weight of Fumed silica and 90% weight of the matrix. For the uniform mixing of fumed silica with Epoxy and hardener, the mixture is prepared using a mechanical stirrer at 1000 rpm for 30 min.

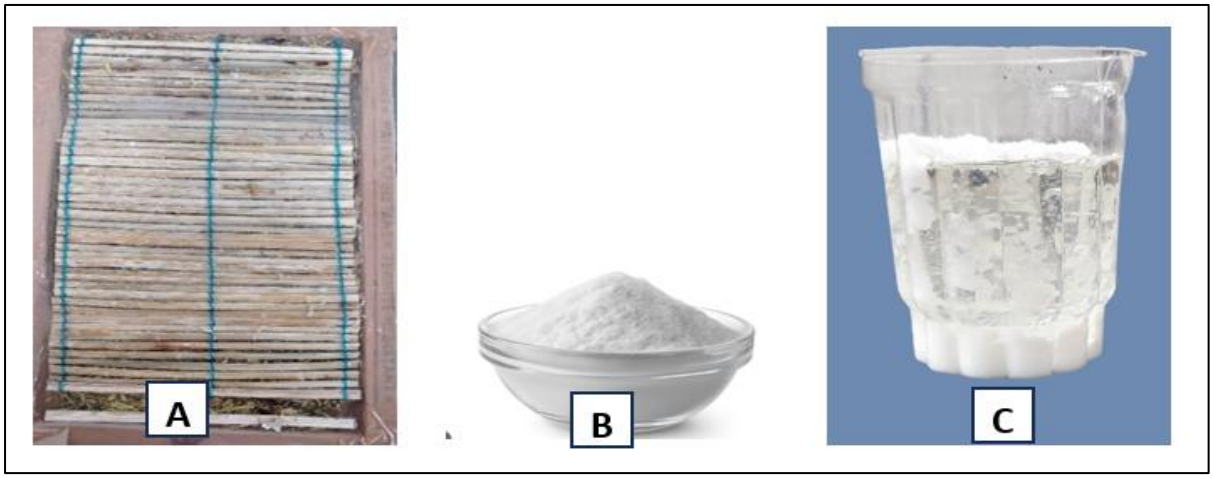

Fig.1. Raw materials for the preparation of Specimens A) Date Palm Fibres, Sugarcane Bagasse and Groundnut shell set up in the mold

(B) Nanoparticles of Fumed silica and (C) Fumed silica added to Epoxy LY556 and hardener HY951

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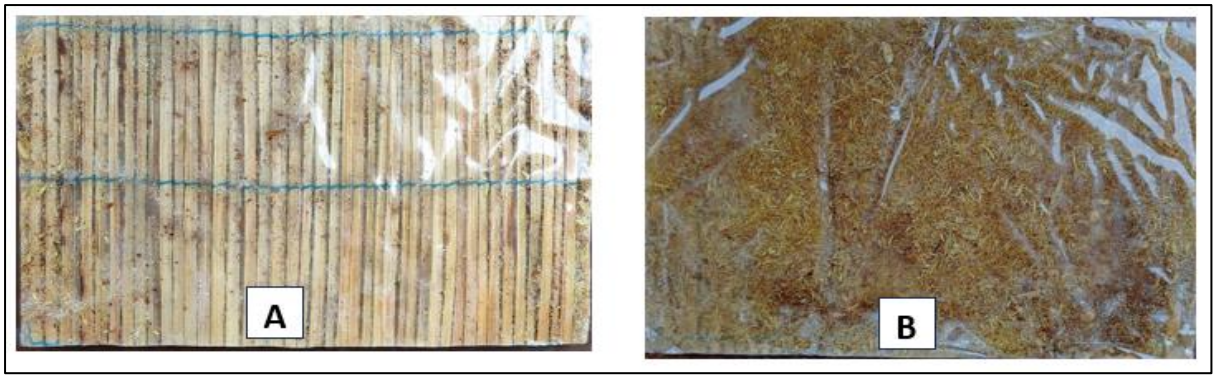

Fig.2 Fabricated Specimen using hand lay-up technique A) Front side of the Specimen B) Backside of the Specimen

Fig-2 shows the front side and the backside of the fabricated specimen from the components as discussed above. After sufficient drying and suitable hardness of the specimen is obtained the obtained specimen is cut out in the shape of a dog bone as shown in **Fig.3**. This is appropriate shape which is used for testing the specimen and observing the properties of the specimen. ASTM 3039 standards were maintained while giving shape to the specimens in both the cases i.e. one without nano-silca and one with nano-silica.

Fig.3 Specimens prepared for UTM testing as per ASTM 3039 Standards A) without Nano-silica B) with the addition of Nano-silica

Fig.4. FE-SEM images captured by Supra 55 (Carl Zeiss, Germany), IIT ISM Dhanbad

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Fig- 4 shows the instrument at IIT- ISM, Dhanbad by which FE-SEM images could be captured for an overview of the inherent properties of the nano-composite samples thus fabricated.

4. Experimental Observations-

Table-1 and **Table -2** give the analysis of the values obtained for the specimens with and without the nano silica particles. Maximum force, tensile stress, tensile strain, compressive displacement etc. are taken into consideration for both the specimens and the comparative values are hence analyzed.

Specimen Label	Maximum Force [N]	Tensile Stress at maximum Force [kPa]	Tensile Strain(Displacement) at Maximum Force [%]	Tensile Strain (Extension) at Break (Standard) [%]
Specimen 1 (without fumed silica)	**890.94**	**5271.85**	**0.46**	**25.03**
Specimen 2 (with fumed silica)	**691.66**	**4940.46**	**0.39**	**1.30**

Table 1: Tensile Characteristics of Specimen 1 and Specimen 2

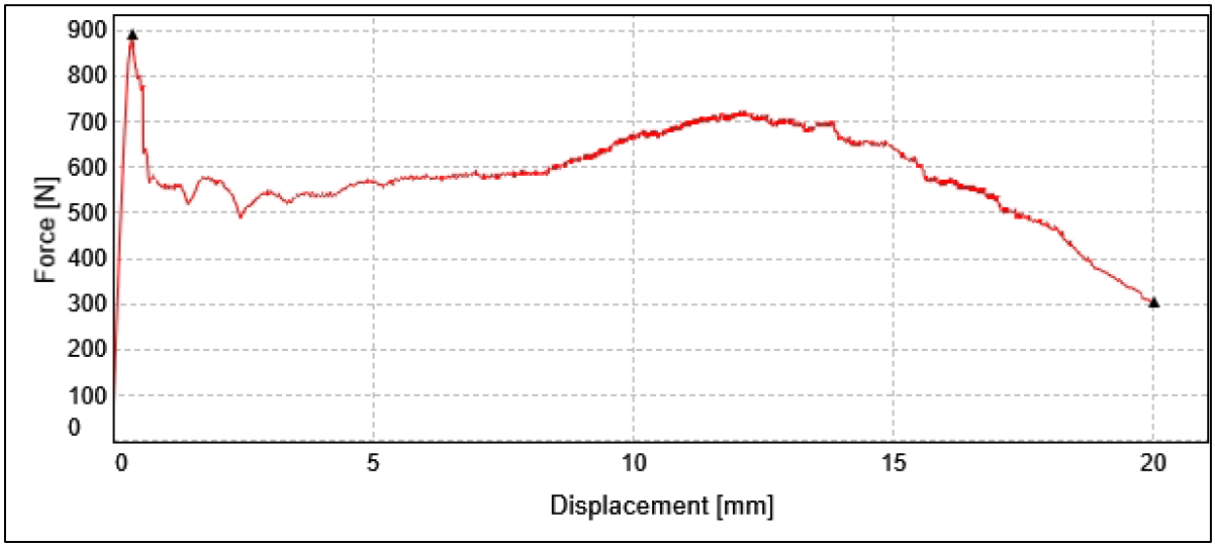

Fig.5.1 Graph for Tensile Force Vs Displacement characteristics of Specimen 1

Fig 5.1 & 5.2, 6.1 & 6.2 and 7.1 & 7.2 give the visual demonstration of the comparative behaviour of the two fabricated samples. The variation in the graphs shows that the incorporation of nano-paticles changes the properties in general whether it may be mechanical properties or microstructural images.

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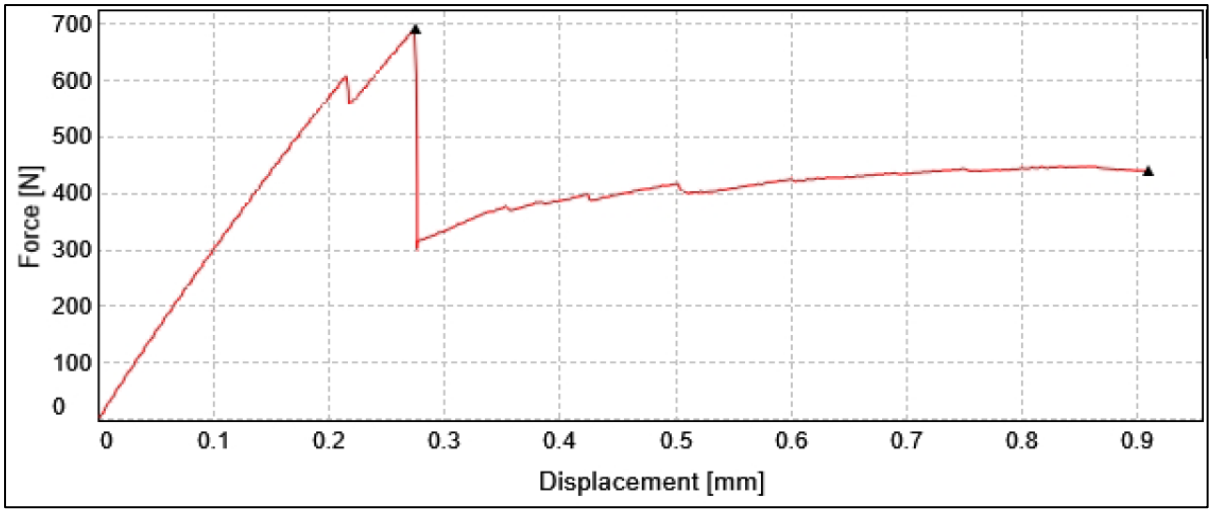

Fig.5.2 Graph for Tensile Force Vs Displacement characteristics of Specimen 2

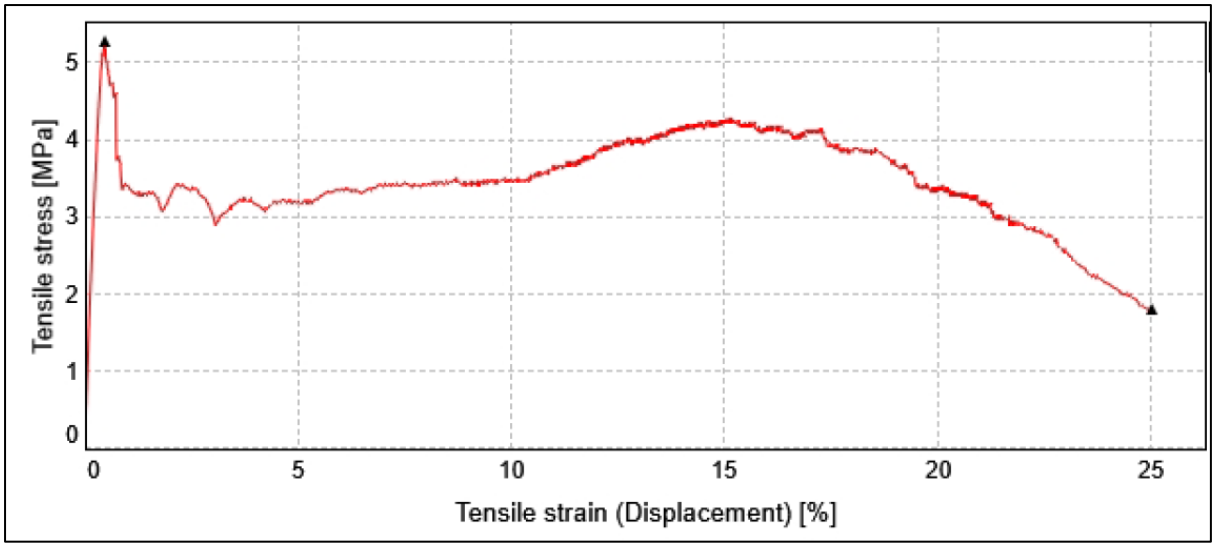

Fig.6.1 Graph for Tensile Stress Vs Tensile Strain characteristics of Specimen 1

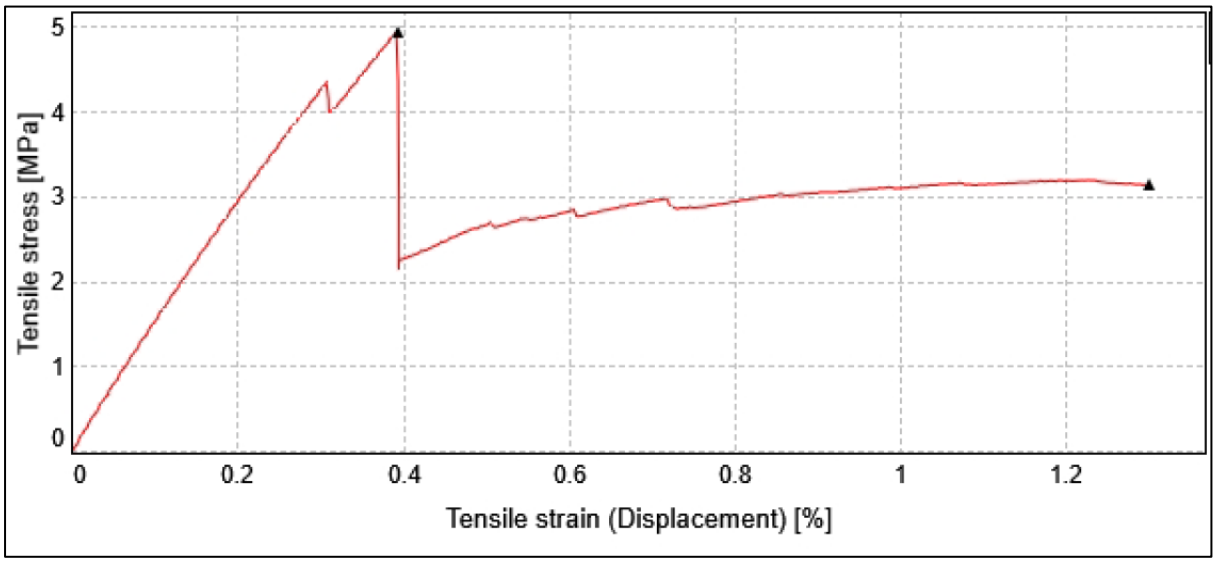

Fig.6.2 Graph for Tensile Stress Vs Tensile Strain characteristics of Specimen 2

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Specimen Label	Displacement at break (Standard) [mm]	Compressive Displacement at Break (Standard) [mm]	Force at Break (Standard) [mm]	Time at Break (Standard) [s]
Specimen 1 (without fumed silica)	**2.07**	**2.07**	**3998.42**	**124.09**
Specimen 2 (with fumed silica)	**3.35**	**3.35**	**3067.25**	**200.98**

Table 2: Compressive Characteristics of Specimen 1 and Specimen 2

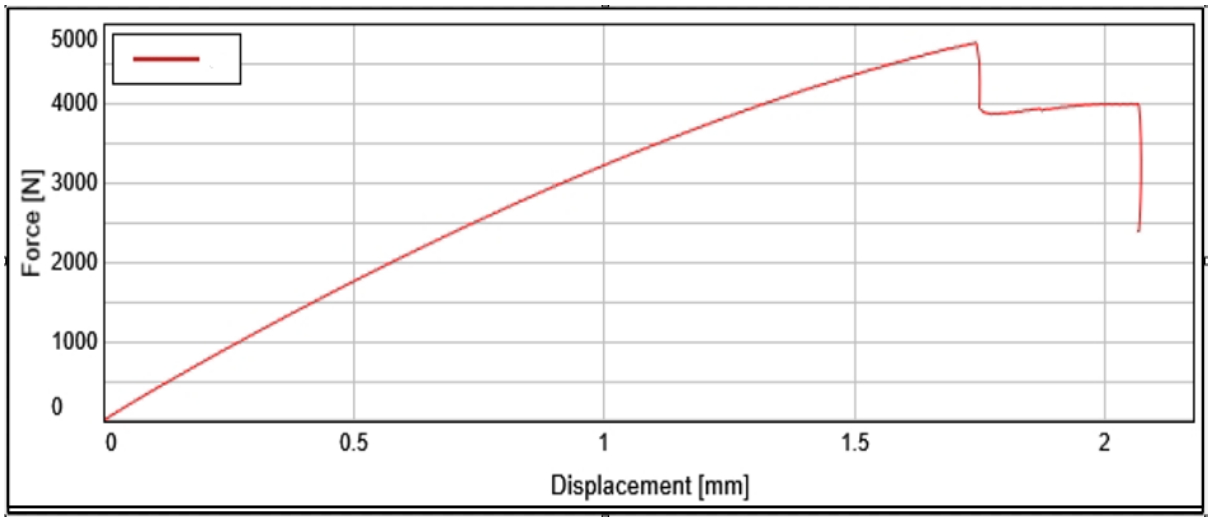

Fig. 7.1. Comparative analysis of Compressive Force Vs Compressive Displacement of Specimen 1

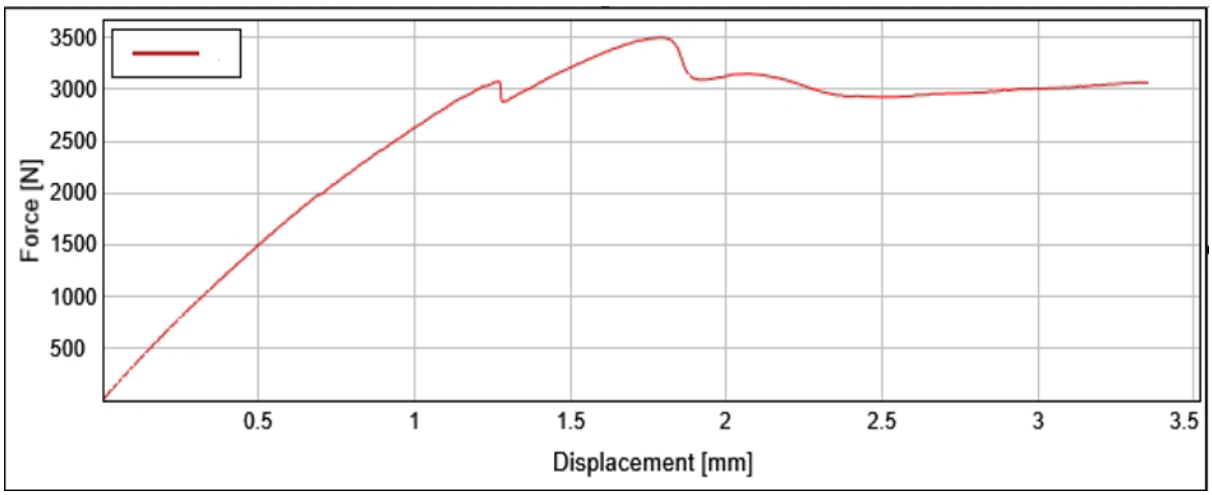

Fig.7.2. Comparative analysis of Compressive Force Vs Compressive Displacement characteristics of Specimen 2

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Fig- 8 demonstrates the FE-SEM Images showing the microscopic characteristics of the two prepared specimens depicted through the FE-SEM images captured at different magnifications. The manifestation of the internal structure allows the understanding of the internal structural properties of the fabricated samples.

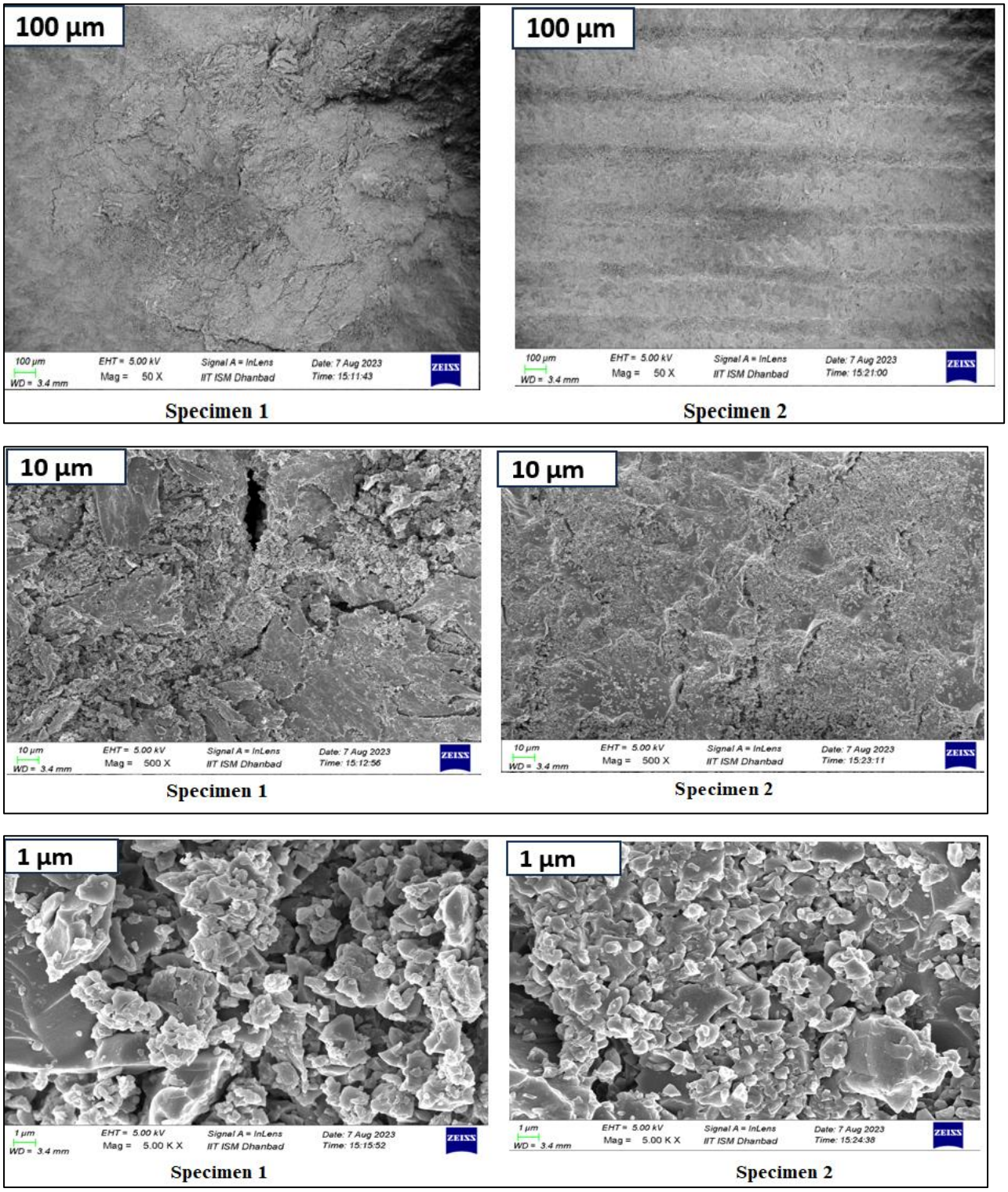

Fig- 8 FE-SEM Images: Microscopic characteristics of the prepared specimens depicted through the FE-SEM images captured at different magnifications

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Fig- 9 shows the microscopic characteristics of the prepared specimens depicted through the FE-SEM images captured at different magnifications. The figure demonstrates the microstructure at various magnification levels and thus allowing the readers to comprehend the internal structure and the properties.

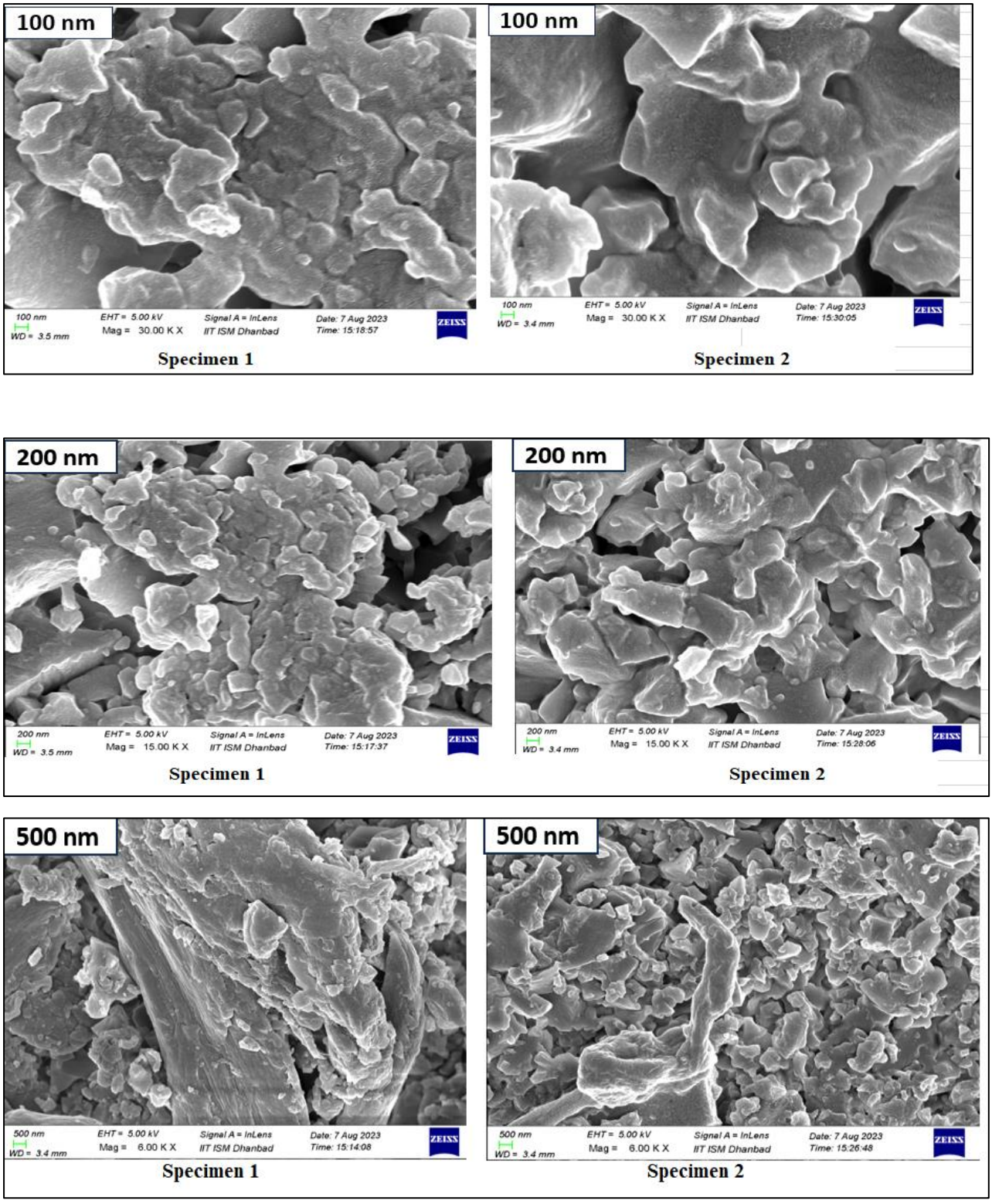

Fig.9. Microscopic characteristics of the prepared specimens depicted through the FE-SEM images captured at different magnifications

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5. Results-

1) There has been a considerable improvement in the physical properties of the natural fibres reinforced composites due to the addition of nano silica. Tensile strength of specimen prepared with hybridized natural fibres was observed to be 5.92kPa/N, and it increased to 7.19kPa/N when fumed silica was mixed with Epoxy resin during the preparation stage.

2) Tensile strain at maximum force also showed slight increase. Specimen without nanoparticles have tensile strain of 0.000516 /N which increased to 0.0005638/N on the addition of nano-silica.

3) Compressive properties when analyzed presented that the compressive displacement at break also increased from 2.07 mm for the specimen without nanofiller to 3.35 mm for the specimen with nanofiller.

4) Surface properties of the composites got enhanced with the reinforcement of nanoparticles. Surface smoothness increased and it is evident from the FE-SEM images that interfacial bonding amongst the matrix and the fibres also improved significantly. Internal Cracks and micro- voids were reduced to a great extent as these silica nanoparticles have high surface area per unit mass.

5) Agglomeration of fumed silica depicted chain like structures in the images which can be reduced by using a suitable solvent to keep them dispersed rather than in the powdered form. Depending on the type of nanoparticles, suitable type of stabilizers and mild reducing agents can also be used to prevent agglomeration.

6. Conclusion-

It is evident from this investigation that nanoparticles of fumed silica have successfully modified the natural fiber composites. This newly developed composite with hybridized fibres and NP’s has the potential to reduce the environmental burden There has been a noticeable improvement in both tensile as well as compression characteristics. Composites reinforced with nano- silica particles have the ability to bear greater stress than composites without reinforcements of nano particles.

Observations from the Field Emission Scanning Electron Microscope (FESEM) images highlight a significant enhancement in the surface morphology of the composites with the addition of nano-silica. The introduction of fumed silica nanoparticles during the fabrication process notably reduces internal cracks and voids in the specimens lacking nanofillers. FESEM images reveal three-dimensional chain-like structures formed by the aggregation of fumed silica, indicating a high specific surface energy.

Future investigations can explore the impact of various other nanoparticles on the properties of natural fiber composites, including water absorption properties, thermal characteristics, and microbial activities. The inclusion of diverse nanoparticles is anticipated to exert a profound influence on the surface morphology, potentially rendering the composite surfaces

 https://doi.org/10.5281/zenodo.13788273

superhydrophobic. Such advancements could find applications across various sectors of the economy.

- **Declaration of Competing Interest**

The authors assert that they do not have any known competing financial interests that could be perceived as influencing the work reported in this paper.

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- **Credit authorship contribution statement**

M.K. Paswan: Conceptualization. Ishita Ghosh: Supervision, Review and Editing Asma Farheen: Writing – original draft, data acquisition, Investigation. Bipin Kumar Chaurasia: Methodology Supervision. Heman Singh Hansda: Data curation.

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