MECHANICAL CHARACTERIZATION OF MULTISCALE SMA FIBER-GRAPHENE NANOPLATELETS/EPOXY COMPOSITES

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ABSTRACT

Fiber reinforced polymer (FRP) composites have been extensively used in various engineering applications due to their lightweights, high strength, and high corrosion resistance. More recently, multiscale composites reinforced with nanoscale materials along with macroscale fibers have received attention of researcher at different disciplines. Graphene nanoplatelets (GNPs) consist of small stacks of individual graphene sheets and possess large surface area with high aspect ratio. They have excellent material properties at a relatively low cost and considered as an ideal filler for composite materials. Shape memory alloys (SMA) are a class of metallic alloys that possess remarkable characteristics such as superelasticity and shape memory effect. Superelastic SMA have been considered as fiber in polymer composites due to their ability to recover their deformation upon removal of load, good energy dissipation capacity and impact resistance.

This study first investigated the tensile behavior of nanocomposites fabricated by GNPs as nanofillers and epoxy (thermoset polymer) as host matrix. Two different epoxy matrices, one ductile and another brittle, were considered. First, an efficient dispersion technique to fabricate GNP/epoxy nanocomposites was explored. The use of ultrasonication alone or in combination with high shear mixing was considered to disperse GNPs into the epoxy matrix. Then, the effect of GNP concentration on the tensile properties of GNP/epoxy composites fabricated by selected three dispersion techniques were studied. A large number of specimens were tested under uniaxial tensile loading and the results were analyzed in terms of tensile strength, fracture elongation, and tensile modulus. Scanning electron microcopy imaging was used to assess the fractured surface of the selected specimens. Next, SMA/epoxy and SMA-GNPs/epoxy composites were produced using a vacuum assisted hand lay-up technique with the selected epoxy resin and GNP content. The developed multiscale reinforced epoxy composites were tested under tensile loading and their full-field strain and temperature behavior were monitored and evaluated using a digital image correlation system and an infrared thermal camera.

It was found that the addition of GNPs into studied brittle epoxy does not provide significant improvements in tensile properties of the developed nanocomposites. On the other hand, considerable enhancements in both tensile strength (up to 40%) and in tensile modulus (up to 55%) was observed when 1 wt. % GNPs are added. In addition, both SMA/epoxy and SMA-GNP/epoxy composites exhibited very good superelastic response with minimal residual deformations and large fracture strains. The addition of GNPs as nanofiller did not alter the tensile characteristics of the multiscale reinforced SMA fiber-based polymer composites, but their potential effects on other mechanical properties such as impact resistance and functional properties such as thermal or electrical conductivity need to be further investigated.

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1. INTRODUCTION

1.1. Background and Motivation

There is a growing demand for advanced composite materials with improved mechanical properties to meet various performance requirements in structural applications. Fiber reinforced polymer (FRP), a composite material composed of a polymer matrix and reinforcing fibers, has been widely used for reinforcing concrete structures. Although various thermosetting polymers such as phenolic, polyester and vinylester resins have been considered as a host matrix in FRP composites, epoxy resin has been one of the most commonly used matrices in fabrication of FRP due to its good and versatile properties. Adding nanofillers to epoxy resins can provide a polymer matrix with improved mechanical properties and additional functional properties.

Carbon nanomaterials exhibit superior mechanical and electrical properties, which make them ideal fillers for polymer nanocomposites [1-3]. The most commonly studied carbon-based nanomaterials has been carbon nanotubes (CNT). Due to their unique structures, CNT possess excellent electrical and thermal properties [4]. However, the poor dispersion and the high cost of CNT are the two critical issues for their use in epoxy nanocomposites [5].

Graphene is one of the stiffest and strongest material available today with ~1 TPa in young’s modulus and ~130 GPa in strength [6]. The unique size and platelet morphology of graphene make these particles especially effective at providing barrier properties, while their pure graphitic composition makes them excellent electrical and thermal conductors. Graphene has an outstanding thermal conductivity of around 5000 $Wm^{-1} K^{-1}$ and very high electrical conductivity [7]. More recently, graphene nanoplatelets (GNPs) that consist of few layers of graphene have emerged as one of the most attractive nanofillers for polymer matrices with an excellent balance between structural properties and cost. GNPs can be found in a variety of geometric features as a function of thickness, diameter and number of atomic layers. GNPs have high aspect ratios and specific surface areas and significantly lower costs compared to CNT. If a good dispersion of GNPs in polymer matrix is achieved, efficient enhancement in mechanical properties can be obtained.

Shape memory alloys (SMA) have been known since the 1950s [8], and their use in various engineering applications have been explored since 1963 [9-12]. SMA broadly can be defined as smart materials that are able to respond to a change in the environmental conditions and then return to their original state after the stimulus is removed. More specifically, SMAs exhibit two unique phenomena: shape memory effect and superelasticity. Both are due to reversible phase transformations between two crystal structures that are austenite and martensite. Superelastic SMAs can undergo martensitic phase transformations as a result of applied load and are capable of recovering permanent strains when the load is removed. On the other hand, shape memory effect (heat-activated) SMAs need a heating and cooling process to gain the initial condition. Both superelastic and shape memory effect SMAs have been utilized in many applications in different fields including biomedical, aerospace, automotive, and construction [13-16].

In addition to their direct use in a variety of applications, SMA materials have also been considered as reinforcement in composite materials. Shape memory effect SMAs have been used as fibers in the development of adaptive polymer matrix composites. In this case, the SMA material is usually incorporated into the epoxy in a pre-strained condition. Raising the temperature produce recovery forces that can be used for prestressing or crack recovery applications. The use of superleastic fibers in epoxy matrix have also been studied due to their potential to enhance damping properties, impact resistance, and ductility of fiber reinforced polymers [17-19]. Since the properties of the composite materials depend on the mechanical properties of the constituent materials and interfacial bonding between these materials, the inclusions of nanofillers in matrix resin can enhance mechanical properties of the SMA fiber reinforced composites.

1.2. Objectives

The objective of this study was to investigate the tensile characteristics of GNP/epoxy nanocomposites and polymer composites reinforced with SMA strands at the micro-scale and with GNPs at the nano-scale. First, GNPs/epoxy composites were fabricated using two types of thermoset epoxy matrices (brittle and ductile). An effective technique to disperse GNPs into epoxy matrix was explored. In particular, the use of ultrasonication alone with different sonication durations and various combination of ultrasonication and high shear mixing was studied. Then, the effects of the GNP concentration on the tensile properties of GNP/epoxy nanocomposites were investigated. A large number of GNP/epoxy specimens were fabricated with selected three dispersion techniques and with different GNP ratio and tested under uniaxial tensile loading. Next, SMA/epoxy and SMA-GNPs/epoxy composites were produced using a vacuum assisted hand lay-up technique with the selected epoxy resin and GNP content. Superelastic NiTi strands with an outer diameter of 0.350 mm were used as fibers at 50% fiber volume ratio to fabricate fiber reinforced polymer composites. Tensile tests were conducted to investigate the characteristics of the developed polymer composites while full-field deformation and temperature fields were recorded.

2. LITERATURE REVIEW

The use of GNPs as nanofiller in epoxy matrix has been studied over the last decade. Their unique size, two-dimensional geometry, stiffness and low thermal interface resistance make GNPs a successful filler to manufacture composite materials with improved mechanical and barrier properties. GNP nanofillers can increase the mechanical properties of the epoxy composites at a considerable level only if the good dispersion is achieved. Development of an appropriate dispersion method of graphene within the epoxy matrix is one of the challenges in fabrication of graphene/epoxy nanocomposites. Improper dispersion causes agglomeration of the graphene in the polymer, leading to composites with reduced tensile strength and modulus where the GNPs acts as a defect. A number of studies have been conducted to study various dispersion techniques for graphene/epoxy nanocomposites and to characterize behavior of epoxy composites reinforced with various forms and contents of GNPs.

Several researchers explored the use of SMAs as fiber in polymer composites. However, no previous study was conducted on the multi-scale reinforced epoxy matrix composites in which GNPs and SMA strands are employed as nano - and micro - scale reinforcements, respectively. The following literature review includes three sections parallel with the objectives of this research following with a summary of literature related with this research. In particular, the relevant works on the following topics are reviewed in this section:

- Methods to disperse GNPs into epoxy matrix
- Tensile behavior of GNP/epoxy composites
- Mechanical characterization of SMA/epoxy composites

2.1. Dispersion of GNPs into Epoxy Matrix

To disperse GNPs into epoxy matrix, three techniques, namely ultrasonication, high shear mixing and three roll milling are commonly used.

The first technique employs an ***Ultrasonic Processor*** to disperse GNPs. Ultrasonic electric generator creates a signal to power a transducer which converts the electric signal to a mechanical vibration. During sonication, cycles of pressure creates thousands of microscopic vacuum bubbles in the solution. The bubbles collapse into the solution in a process known as cavitation. This causes powerful waves of vibration that release an enormous energy force in the cavitation field, which disrupts molecular interactions such as interactions between molecules of water, separates clumps of particles, and facilitates mixing.

High Shear Mixing (HSM) is another technique for nanoparticle dispersion. High shear mixers consist of a rotor that turns at high speed within a stationary stator. Typically, a rotor includes a single set of four blades. As the rotating blades pass each opening in the stator, they mechanically shear particles at high velocity into the surrounding mixture, creating intense hydraulic shear. As fast as material is expelled, more is drawn into the bottom of the rotor/stator generator, which promotes continuous flow and fast mixing. At the end, homogeneous mixture can be obtained.

The third technique is ***Three-Roll Milling (TRM)***, which is also known as calendering. A three-roll milling machine generates shear forces through three horizontally positioned rolls rotating in opposite directions and different speeds relative to each other. Material is fed between the feed roll and the center roll. In the in-running nip experiences very high shear force occurs due to the different rotation speeds of the two rolls. At the end, a knife blade scrapes the processed material off the apron roll. This milling cycle can be repeated several times to maximize dispersion.

In the literature, one of the above-mentioned techniques have been used alone or in combination with one other in order to disperse GNPs into epoxy matrix. The dispersion methods used in some of the recent studies are introduced below.

The Effect of Shear Mixing Speed and Time on the Mechanical Properties of GNPs/Epoxy Composites (Pullicino et al. 2016) **[20]**

The researchers in this paper aimed to examine the effect of shear mixing speed and time on the mechanical properties of GNPs/epoxy composites. For this purpose, only high shear mixer was used at different rotating speed for different lengths of time. The epoxy resin was shear mixed for two time durations (1 and 2 h) and five different speeds (1000 to 5000 rpm), making in total ten samples. The resin was weighed and curing agent was added in the appropriate ratio and stirred at 1000 rpm for 3 min. The mixture was poured into silicon tensile shaped molds and cured in an oven for 2 h at 80 °C followed by 8 h at 140 °C. The results showed them that the high shear mixing speed and time considerably affect the size of agglomerates, which has an impact on the mechanical properties of the composite. The minimum average size of agglomerate was recorded for the specimens fabricated at 3000 rpm and 2 h of mixing.

Influence of graphene nanoplatelets on curing and mechanical properties of graphene/epoxy nanocomposites (Prolongo et al. 2015) **[21]**

Dispersion of GNPs in this study was obtained through mechanical stirring followed by sonication. Dispersion was conducted at 80 ^{o}C with stirring at 300 rpm for 30 min, and then sonicated 60 min with a power of 400 W and amplitude of 50 %. The temperature did not exceed 80 ^{o}C. After that, the mixture was degassed under vacuum (40 mbar, 15 min). The curing agent was added at 80–85 ^{o}C and mixed for 5 min. Finally, the mixture was poured in aluminum molds of suitable dimensions and cured in an oven for 2 h at 120 ^{o}C followed by 1 h at 180 ^{o}C under atmospheric pressure.

Mechanical and Electrical Properties of Graphene Nanoplates and Carbon-Nanotubes Hybrid Epoxy Nanocomposites (Moosa et al. 2016) **[22]**

In this study, researchers prepared nanocomposites by direct mixing of nanofiller with epoxy resin using high speed mixer at 3000 rpm for 15 min. Then, ultrasonic processor was used in order to disperse nanofillers into epoxy resin at 200W power and 25 kHz frequency in an ice-water for 20 min. The hardener was then added with the appropriate ratio. The mixture was then centrifuged at speeds of 3,000 rpm for 2 min. to remove the bubble and was then poured into the mold and left for 24 hours to complete the curing process. The nanocomposites were then heated for three hours in an oven at a temperature of 80°C for post-cure.

Mechanical properties and adhesive behavior of epoxy-graphene nanocomposites (Salom et al. 2017) **[23]**

In this study, dispersions of graphene nanoplatelets were obtained through mechanical stirring at 700 rpm for 10 min. at 70 ^{o}C. Then, sonication process was applied for 60 min with a power of 400W and amplitude of 50%. The temperature did not exceed 40 ^{o}C. Once the dispersions were obtained, the appropriate amount of hardener for a stoichiometric ratio (weight fraction prepolymer/ hardener = 100/23) was added and mixed for 5 min, and then the samples were degassed under vacuum (40 mbar) at 80 °C for 15 min. The final mixture was poured into aluminum molds, previously treated with mold release product, and were cured at 140 °C for 8 h under atmospheric pressure.

Epoxy/graphene platelets nanocomposites with two levels of interface strength (Zaman et al. 2011) **[24]**

In this study, GNPs was suspended in 100 g THF (tetrahydrofuran) using a metal container. The container was then covered and went through a sonication process of 30 min below 30 C. Epoxy resin was added and mixed by a mechanical mixer at ~100 ^{o}C for 60 min for two purposes:

achieving a homogeneous dispersion of GNP in epoxy matrix, and vaporizing THF. When hardener was added, mixing was controlled at ~40 ^{o}C for 1 min to avoid premature curing, followed by a vacuum oven-degassing process to remove bubbles. The final mixture was poured into a rubber mold and cured first at 80 °C for 3 h followed by 120 ^{o}C for 12 h under atmospheric pressure.

Advantages and disadvantages of the addition of graphene nanoplatelets to epoxy resins (Prolongo et al. 2014) **[25]**

In this research, GNPs dispersion on epoxy resin was carried out through a combination of different dispersion techniques. First, an ultrasonication process was applied for 45 min. An amplitude of 50% was used with the sonication power of 400W. Then, the mixture was treated in a three-roll milling with a rolling speed of 250 rpm. The calendering process was applied for four consecutive times. The time of each mill-rolling cycle was approximately 5 min. Afterwards, the GNPs/epoxy mixture was degassed in vacuum at 80 ^{o}C for 15 min. Then, the hardener was added into the mixture in appropriate ratio at 80 ^{o}C. The curing treatment consisted of heating at 140 ^{o}C for 8 h. The cured samples were cooled slowly to room temperature inside the oven.

The reinforcing effect of polydopamine functionalized graphene nanoplatelets on the mechanical properties of epoxy resins at cryogenic temperature (Wu et al. 2016) **[26]**

The researchers of this article dispersed GNPs first into acetone and then epoxy resin. 0.25 g of GNPs was dispersed in 100 mL acetone under ultrasonication for 30 min. 200 g of the epoxy resin was added to the suspension and treated by ultrasonication for another 30 min. The resulted mixture was then put into an oven at 80 ^{o}C for 24 h to remove acetone. Afterwards, 50 g of the hardener was added to the mixture and stirred for 10 min. The resultant suspension was degassed with a vacuum pump to eliminate air bubbles and residual acetone. After that, the mixture was transferred to an open mold and cured at 80 ^{o}C for 8 h, then 130 ^{o}C for another 8 h.

<u>Mechanical properties and thermal conductivity of graphene nanoplatelet/epoxy composites (Wang et al. 2014)</u> **[27]**

Acetone was also used for this article. The GNPs was pre-dispersed in acetone (concentration of GNPs is 15 mg/ml) by ultrasonic processor at 90 W for 2 h in an ice bath. After that, a weighed amount of epoxy was added to the GNPs/acetone mixture and stirred with a magnetic stirrer on a hot plate until the epoxy was completely dissolved and then sonication treat was applied for 30 min at 100 W in an ice bath. After sonication, the mixture was heated at 60 ^{o}C on a hot plate under stirring until the acetone evaporated. The GNPs/epoxy mixture was further processed using a three-roll mill calendaring at room temperature for 15 passes with a rotation speed of 250 rpm. The final product had the appearance of a homogeneous, well-dispersed mixture.

Table 1 provides a summary of the dispersion techniques used in the literature in fabrication of GNP/epoxy nanocomposites.

Table 1: Summary of dispersion techniques

Study	Dispersion Technique Used
Pullicino et al. 2016	60 & 120 min HSM
Prolongo et al. 2015	30 min HSM + 60 min Ult.
Moosa et al. 2016	15 min HSM + 20 min Ult.
Salom et al. 2017	10 min HSM + 60 min Ult.
Zaman et al. 2011	30 min Ult. + 60 min HSM
Prolongo et al. 2014	30 min Ult. + 60 min TRM
Wu et al. 2016	30 min Ult. + 30 min Ult.
Wang et al. 2014	120 min Ult. + 60 min MS

2.2. Tensile Behavior of GNPs/epoxy Composites

There are several types of GNPs commercially available as well as epoxy systems. Each epoxy system may have different mechanical characterization and each GNPs type may affect the mechanical properties of composites in a different manner. This section provides a review of findings of recent studies on the tensile behavior of GNPs/epoxy composites.

Mechanical properties of graphene nanoplatelet/epoxy composites (King et al. 2012) **[28]**

In this study, researchers fabricated neat epoxy (EPON 862 with Curing Agent W) and 1–6 wt. % GNPs in epoxy composites. To produce GNP/epoxy composites, the required amount of GNPs was added to epoxy and mixed using a high shear mixer at 2500 rpm for 40 min. The fabricated specimens were tested for tensile properties. The results showed that the tensile modulus increased from 2.72 GPa for the neat epoxy to 3.36 GPa for 6 wt.% GNPs in epoxy composite. However, the ultimate tensile strength decreased from 77.6 MPa for the neat epoxy to 35.5 MPa for the formulation containing 6 wt.% GNPs in epoxy. Similarly, the strain at ultimate tensile strength decreased from 8.0 % for the neat epoxy to 1.5 % for the GNP/epoxy composite.

Mechanical properties and tensile fatigue of graphene nanoplatelets reinforced polymer nanocomposites (Shen et al. 2013) **[29]**

In this study, the mechanical properties of GNPs/epoxy nanocomposite, such as ultimate tensile strength and flexure properties, were investigated. Various concentrations of GNPs (0, 0.25, 0.5, 1, and 1.5 wt. %) were uniformly dispersed into epoxy resin. GNPs were mixed with epoxy resin for 90 minutes using a mechanical mixer and then vibrated by ultrasonication for 90 minutes to enable uniformly dispersed GNPs throughout the epoxy solution. The tensile strength of nanocomposites with 0.25 wt. % GNPs showed the best enhancement with 20 % of increase in strength compared to neat epoxy. The strength showed a decrease as GNPs content increased to

0.5, 1, and 1.5 wt. % because the GNP aggregates would sterically hinder polymer flow, thereby resulting in the formation of defects.

Mechanical properties of graphene nanoplatelet/epoxy composites (Klimek et al. 2015) **[30]**

Researchers in this study observed that the addition of different types of GNPs to epoxy matrix increases the tensile modulus of epoxy. Test specimens were fabricated using a 2 in diameter disperser blade in a high shear mixer at 2500 rpm for 40 min. The modulus for the neat epoxy was measured to be 2.72 GPa. The addition of 6 wt. % GNPs with the grades of M-15, M-5 and C-300 in epoxy increased the tensile modulus to 3.36 GPa, 3.35 GPa and 3.10 GPa, respectively. The stress and strain for the M-15 and M-5 GNPs in epoxy decreased rapidly as more GNPs was added. The stress and strain for C-300 GNPs stays constant until about 4 wt. % and then begins to decrease slowly as more GNPs is added. The ultimate tensile stress and strain at ultimate tensile stress for neat epoxy was measured to be 77.6 MPa and 8.0 %, respectively. For 4 wt. % of M-15, M-5 and C-300 GNPs in epoxy, maximum stresses and strains were measured to be 41.9 MPa with 2.2% strain, 43.9 MPa, 75.8 MPa and 4.6%, respectively.

Effect of functionalization of graphene nanoplatelets on the mechanical response of graphene/epoxy composites (Moghadam et al. 2014) **[31]**

Researchers in this study used functionalized GNPs which was obtained by bonding a silane agent to its structure. Nanoparticles were dispersed in the epoxy resin using a three-roll mill and then the hardener was added to the GNP-resin slurry and mixed for 15 min using a mechanical stirrer at 150 rpm. Nanocomposites with different weight contents (i.e., 0.25, 0.5 and 1 wt. %) of GNPs were prepared and their mechanical properties were investigated. It was observed that by inclusion of 0.25, 0.5 and 1 wt. % of GNPs in the epoxy, the ultimate strength of nanocomposites increased by an average amount of 15%, 38% and 21%, respectively. Thus, it could be concluded that the composites having 0.5 wt. % GNPs provided the best results in ultimate strength. On the other hand, at the lowest GNPs content (i.e., 0.25 wt. %), the elastic modulus of nanocomposites did not vary noticeably compared to that of the neat epoxy. By increasing the nanoparticle contents from 0.25 wt. % to 0.5 wt. %, an average growth of 14 % in the elastic modulus was observed.

Effects of graphene nanoplatelets and graphene nanosheets on fracture toughness of epoxy nanocomposites (Shokrieh et al. 2014) **[32]**

In this paper, the tensile behavior of GNPs/epoxy composites were studied with nanofiller concentrations of 0.05, 0.1, 0.25, 0.5 and 1 wt. %. Epoxy resin was mixed with the nanoparticles and stirred for 10 min at 2000 rpm, and then the mixture was sonicated with 14 mm diameter probe sonicator at an output power of 200 W. The maximum of the tensile strength was found at 0.25 wt. % of GNPs (73.9 MPa) showing a rise of 23% in comparison with the neat epoxy (60 MPa). Researchers of this study suggested that a major reason for decreasing trend of the strength in higher filler contents, that is, 0.5 and 1 wt. %, can be attributed to increasing stress concentrations in un-dispersed or agglomerated GNPs. Agglomerates reduce the level of stress transfer from matrix to individual platelets and introduce larger stress concentration regions. The tensile modulus of the neat epoxy enhanced by about 4.5 % (from 2.50 GPa to 2.61 GPa) with addition of 0.1 wt. % GNPs. Increasing the filler concentration resulted in further increase in modulus, and the highest value of modulus was achieved at 0.5 wt. % of GNPs (2.76 GPa) showing nearly 10% improvement.

Table 2 provide a summary on the findings of previous studies on tensile behavior of GNP/epoxy nanocomposites.

Table 2: Summary of tensile response improvements in GNP/epoxy nanocomposites

Study	**Dispersion Technique**	**Used GNP Ratios (wt. %)**	**Max. Tensile Improvements**	
			Strength	**Modulus**
King *et al. 2012*	40 m. HSM	1, 2, 3, 4, 5, 6	- 54 % ***(at 6% M-15)***	+ 23 % ***(at 6% M-15)***
Shen *et al. 2013*	90 m. HSM 90 m. Ult.	0.25, 0.5, 1, 1.5	+ 20 % ***(at 0.25% GNP)***	-
Klimek *et al. 2015*	20 m. HSM	1, 2, 3, 4, 5, 6	- 2 % ***(at 4% C-300)***	+ 23 % ***(at 6% M-15)***
Moghadam *et al. 2014*	TRM 15 m. HSM	0.25, 0.5, 1	+ 38 % ***(at 0.5% M-15)***	+ 15 % ***(at 0.5% M-15)***
Shokrieh *et al. 2014*	10 m. HSM Ult.	0.05, 0.1, 0.25, 0.5, 1	+ 19 % ***(at 0.25% M-15)***	+ 15 % ***(at 0.5% M-15)***

2.3. Mechanical Characterization of SMA/epoxy Composites

Over the past decades, there has been a great interest in SMA materials in structural applications, however, the studies on the use of superelastic SMAs as fibers in polymer composites have been limited. Previous studies on the mechanical characterization of SMA/epoxy composite are reviewed below.

Characterization of superelastic shape memory alloy fiber-reinforced polymer composites under tensile cyclic loading (Daghash et al. 2016) **[33]**

In this study, uniaxial SMA-FRP composites were fabricated and tested under cyclic loads to investigate their mechanical properties. The composite specimens with three SMA fiber volume ratio (3.0 %, 4.9 %, and 9.9 %) were manufactured and tested under incrementally increased uniaxial cyclic tensile loads in a force-controlled mode. The researchers found that FRP composites reinforced with different volume ratios of SMA fiber can fully recover large strains upon unloading and attain an ultimate tensile strain between 10 and 12 %. For the specimen with 3.0 % SMA fiber volume ratio, a strain recovery with minimal residual deformations was observed. The specimen exhibited full strain recovery at 3.1 % strain loading and corresponding stress of 47.1 MPa for SMA-FRP with 4.9 % fiber volume ratio. For the specimen with 9.9 % SMA fiber volume ratio, a strain recovery with minimal residual deformations was observed at 6.8 % with corresponding stresses around 70 MPa. It was observed in this study that increasing fiber volume ratio significantly improved superelastic characteristics of the composites.

Fabrication and Cyclic Behavior of Highly Ductile Superelastic Shape Memory Composites (Zafar et al. 2014) **[34]**

This paper investigated the fabrication and cyclic behavior of SMA-FRP that could be used as seismic reinforcement for concrete structures. The new composite comprises a high elongation resin matrix, embedded with superelastic NiTi shape memory alloy (SMA) wires as primary reinforcement. The SMA wires were used either with or without the addition of conventional fibers. The experimental program carried out in this study starts with the training of SMA wires, and the investigation of the hysteretic behavior of several types of resin. Two types of SMA-FRP composite material were then fabricated and tested under uniaxial tensile cyclic loading. The first type of composite was reinforced with 100% SMA wires, while the second type was reinforced with hybrid fibers made of SMA and glass-FRP. Results showed that 100% SMA-FRP composite specimens (FRC) provide high ductility, energy dissipation, and elongation properties while maintaining negligible residual strains. On the other hand, SMA-FRP hybrid composite (PRC) specimens showed higher stiffness and strength behavior compared to 100% SMA-FRP composite specimens while exhibiting reasonable elongation and hysteretic properties.

Damping, tensile, and impact properties of superelastic shape memory alloy (SMA) fiber-reinforced polymer composites (Raghavan et al. 2009) **[35]**

Researchers in this article demonstrated successful manufacturing of unidirectional superelastic fiber reinforced composites with pre-strained fibers and good fiber–matrix bonding. Tensile and instrumented impact testing were carried out to evaluate improvements in mechanical properties and toughness of the composites. Appreciable improvement was observed in damping, tensile, and impact properties of the polymer matrix due to reinforcement with superelastic SMA fibers, highlighting the advantages of their use in polymer composites. They found that the critical stress for the phase transformation from the austenite, in the presence of thermal martensite, to stress-induced martensite was 515 MPa. At the critical stress of 128 MPa, the matrix separated from the fibers bridging them, resulting in a drop-in stress. They observed that the increase in stress from this point was marginal, resulting in a plateau similar to that observed for the SMA fiber. However, the number of matrix cracks increased within the gage length of the test coupon during this period, which confirms the good bonding between the fiber and the matrix. At about 8% strain, the stress started to increase and the matrix cracking continued until 9% strain.

2.4. Summary of Literature Review

It is clear from the summarized papers above, there is no commonly preferred and used dispersion method to disperse GNPs into epoxy matrix. Various amplitudes and mixing durations have been used with different devices to disperse GNPs in different epoxy matrices. Although a single technique such as ultrasonication was used for the dispersion in different studies, in more recent studies hybrid mixing methods that consist of a combination of ultrasonication, high shear mixing and three-roll milling methods have been used. Depending on the types of GNPs and epoxy matrices, the duration of mixing using a single device (i.e. ultrasonication or high shear mixer) varies from as low as 20 min and goes up to about 3 hours. For the studies where both ultrasonicator and high shear mixer were used, a total time of 1.5 hours has been mostly used with various time durations of operation for each individual device.

A number of studies explored the effects of GNPs on the tensile properties of the epoxy matrix by fabricating and testing specimens fabricated with different concentrations of GNPs. Different types of GNPs were mixed with different host matrices, and an increase in mechanical properties was observed with the addition of GNPs up to certain concentration. As summarized above, Moghadam et al. 2014 achieved large improvements in tensile behavior, i.e. 38 % increase in tensile strength with 15 % increase in tensile modulus, with the addition of 0.5 wt. % GNPs. On the other hand, King et al. 2012 observed 54 % decrease in tensile strength with 6 wt. % of GNPs, however, in the same study they found 23 % increase in tensile modulus with the same GNPs concentration. It can be inferred from these studies that there is no regular pattern in tensile behavior of epoxy with the addition of GNPs into epoxy matrix.

In current study, the multiscale reinforcement of an epoxy matrix using GNPs as nanofillers and SMAs as fiber is investigated. The next section describes the materials used in this study.

3. MATERIALS

For this research study, two types of matrix materials used; one brittle epoxy and one ductile epoxy. Two different materials were studied in the epoxy matrix; Graphene nanoplatelets (GNPs) and Shape Memory Alloys (SMA). The following sections covers the materials in more detail.

3.1. Matrix Materials

Brittle and ductile epoxy matrices were studied for this research.

3.1.1. Ductile Epoxy

635 Thin Epoxy System was used as ductile epoxy matrix which is based on Bisphenol-A and supplied by US Composites, Inc. The chemical structure of bisphenol-A is shown in Figure 1.

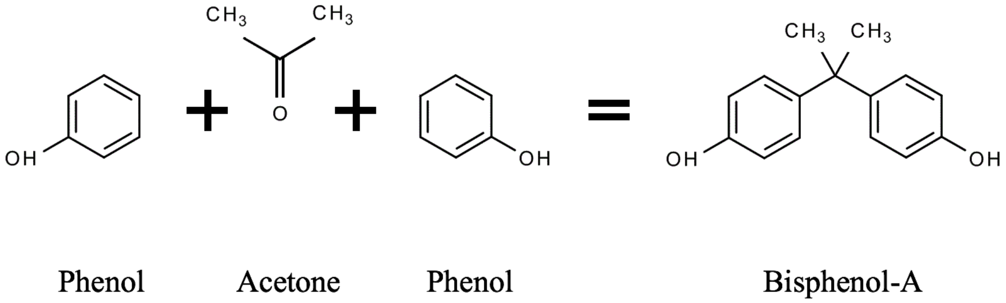


Figure 1: Chemical structure of bisphenol-A

This ductile epoxy has a syrup-like consistency which generates fast wet-out and easy application of any reinforcement. With the addition of hardener in the weight ratio of 2:1, will produce a low viscosity, semi-clear, low odor epoxy that is ideal for host matrix of composite. The ductile epoxy has a viscosity of 600 cps at 25 ^{o}C / 77 ^{o}F.

3.1.2. Brittle Epoxy

Similarly, brittle epoxy used for this study is also based on bisphenol-A, but diglycidylether of Bisphenol-A. The commercial name of this epoxy system is EPOTUF® 37-140 epoxy resin and EPOTUF® 37-650 hardener was used with a weight ratio of 100:70 and provided by Reichhold. Brittle epoxy has a higher viscosity value (12,500 cps at 25 ^{o}C) compared to ductile one. Unlike ductile epoxy, brittle epoxy has an organochlorine compound named as epichlorohydrin which combines with bisphenol-A to form diglycidylether of Bisphenol-A. Figure 2 shows the chemical structure of diglycidylether of Bisphenol-A.

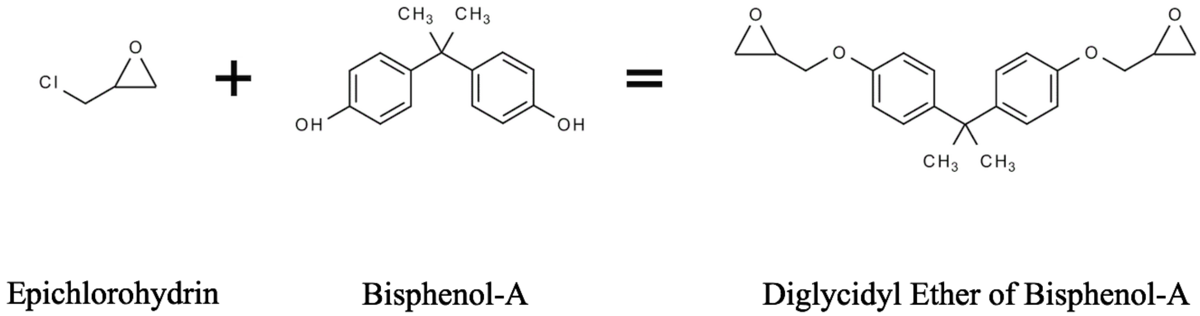


Figure 2: Chemical structure of diglycidylether of bisphenol-A

3.2. Fillers

3.2.1. Graphene Nanoplatelets (GNPs)

Graphene is an allotrope of carbon consisting of a single layer of carbon atoms arranged in an atomic-scale hexagonal lattice. Graphene nanoplatelets (GNPs) are short stacks of graphene sheets. A graphene sheet is defined as a single layer of graphite. Figure 3 represents a single layer of graphene and GNPs.

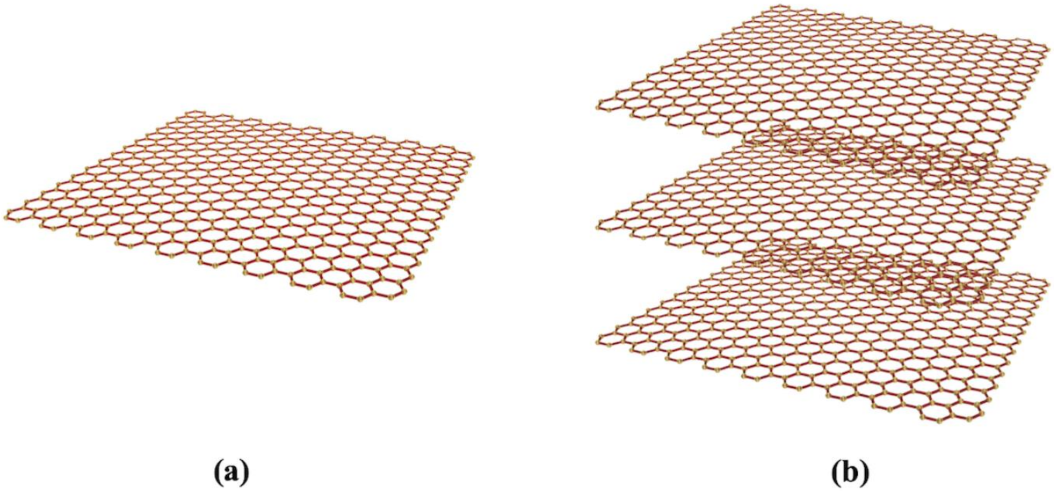


Figure 3: (a) A single layer of graphene, (b) GNPs

GNPs are available in many different particle diameters, thicknesses and surface areas. Particle diameter of GNPs varies from 2 μm to 25 μm with the thickness from 1-2 nm to 15 nm. For this research, GNPs were obtained from XG Sciences, Inc. with the commercial name of Grade M-25 which indicates the particle diameters of 25 microns. Grade M-25 GNPs have a typical surface area of 120 to 150 m^2/g and an average thickness of 6 to 8 nm which gives the maximum aspect ratio among the available types of GNPs.

3.2.2. Shape Memory Alloys (SMAs)

The reinforcing fibers used in this study were 0.35 mm diameter superelastic SMA strands consists of seven 0.117 mm diameter wires wrapped helically, as shown in Figure 4. The strands were obtained from Fort Wayne Metals, Inc.

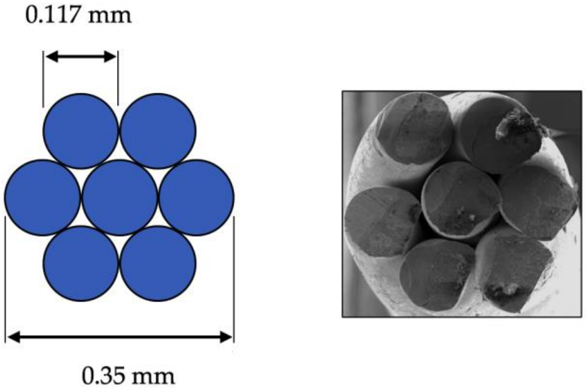


Figure 4: Cross-section of 0.35 mm diameter SMA strands

According to the manufacturer, the SMA strands have a yield stress of 692 MPa, tensile strength of 1284 MPa, and ultimate elongation of 12.8%. Superelastic SMA strands mostly comprise of Nickel (Ni) and Titanium (Ti) but they also contain small concentrations of Carbon (C), Cobalt (Co), Nitrogen (N) and Oxygen (O). The chemical composition of SMA strands are represented in Table 3.

Table 3: Chemical composition of SMA strands

Element	**Weight %**
Nickel (Ni)	54.51
Titanium (Ti)	Balance
Carbon (C)	0.043
Cobalt (Co)	1.38
Nitrogen (N)	0.003
Oxygen (O)	0.031

4. EFFECT OF DISPERSION TECHNIQUE ON TENSILE RESPONSE OF GNP-EPOXY NANOCOMPOSITES

GNPs are made out of individual layers of graphene that are bonded by van der Waals forces. These van der Waals forces between the fillers restrain the good dispersion which can result in uneven, non-homogenous dispersion. Mechanical properties of the composites can easily be decreased with poor dispersion. Thus, in order to obtain homogeneous and stable dispersion of the nanofillers in the polymer matrix, a proper dispersion technique was explored.

In particular, the dispersion of GNPs in the epoxy matrix was analyzed with ultrasonication and high shear mixer. First, only ultrasonication was used to disperse GNPs in epoxy matrix. The effect of ultrasonication duration in dispersing GNPs into brittle and ductile epoxy was analyzed. Then, a combination of ultrasonication and high shear mixing was applied with various durations. The dispersion of GNPs into first epoxy resin or first into hardener was studied. The effect of using acetone in the dispersion was also analyzed. The resultant mixtures were analyzed using Optical Microscope and cast into plastic molds and tested for tensile behavior. The proper dispersion technique was decided based on the results. The following sections cover the development of dispersion technique in detail.

4.1. Dispersion of GNPs into Epoxy Matrix Using Ultrasonication

4.1.1. Effect of Ultrasonication Duration

An ultrasonic processor was used for dispersion of GNPs into epoxy matrices. Figure 5 shows the ultrasonic processor (Cole-Parmer 750-Watt Ultrasonic Homogenizer) used in this study. In order to evaluate the effect of ultrasonication time on dispersion, 30 min, 1 h, 2 h and 3 h of ultrasonication durations were applied. Both brittle and ductile epoxies were used for the dispersion by ultrasonication with an amplitude of 40 %. Since the temperature of the mixture was observed to increase a lot due to the vibration of microtip, an ice bath was used to prevent the temperature increase as shown in Figure 5.

Figure 5: Ultrasonic processor

Since the interfacial bond between GNPs and epoxy matrix is really important for stress and strain transfer from matrix to nanofiller and vice-versa, an optimum ultrasonication duration needs to be determined. Optical microscope images of GNP/epoxy mixtures before the addition of hardener (i.e. in liquid form) are provided in Figure 6 for ductile epoxy. Figure 6(a) shows the optical image of the 30 min ultrasonication mixture and it was observed that the mixture contains particles having 25 μm surface area. Increase in the ultrasonication time generally resulted in decrease in particle sizes of GNPs. The particle size after 2 h and 3 h of ultrasonication was observed to be 4 ± 0.5 μm, shown in Figure 6(c) and 6(d) and a very slight decrease in the particle size was observed after 1 hour. Therefore, an ultrasonication duration above 1 hour can be suggested for better dispersion. Tensile tests were conducted to further investigate the ultrasonication time period on tensile strength of the composites, which is discussed in the next section.

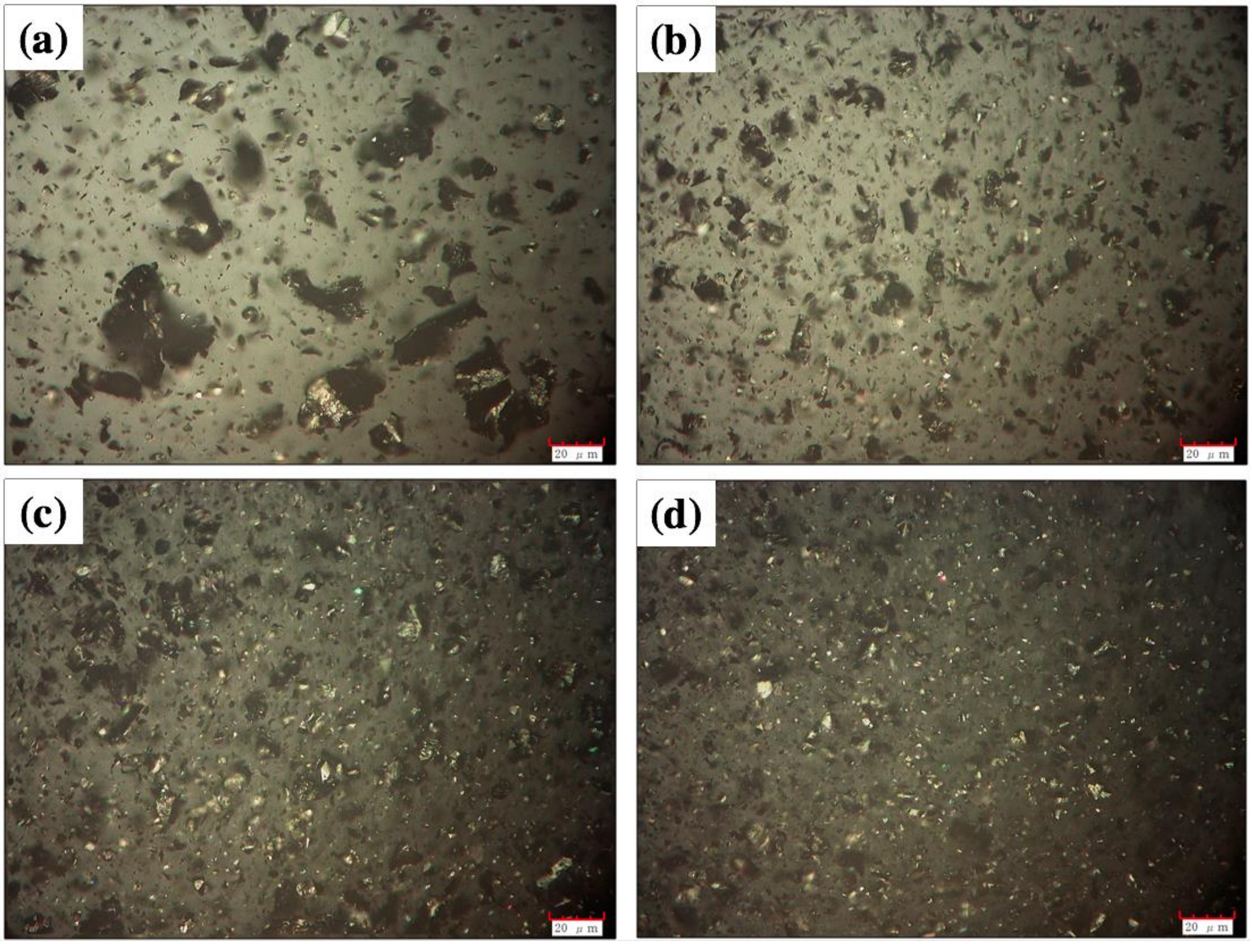


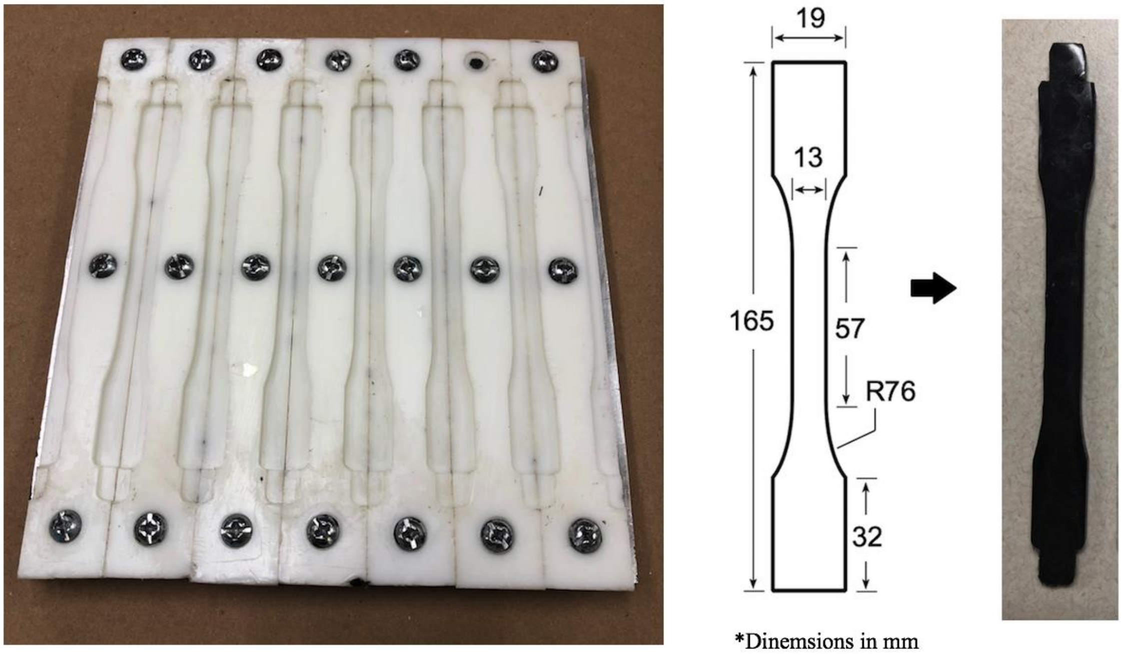
Figure 6: Optical microscope images of GNP-epoxy nanocomposites for ultrasonication time of (a) 30 min, (b) 1 hour, (c) 2 hours, and (d) 3 hours

4.1.2. Fabrication of Tensile Test Specimens

Specimens for the tensile test were fabricated by using both ductile epoxy and brittle epoxy. The fabrication processes for ductile epoxy were carried out using following steps. 0.25 wt. % of GNPs were added to the ductile epoxy and mixed using the ultrasonic processor at an amplitude of 40 % for 2 hours. The resulting mixture was degassed inside a vacuum oven (29” Hg pressure) at 90 ^{o}C for 20 min. To this end, a vacuum pump was connected to the vacuum oven in order to clean air inside the oven as shown in Figure 7. Then, the mixture was mechanically mixed with the hardener for 3-5 min. using the ratio of 2:1.

Figure 7: Vacuum oven and vacuum pump

The mixture was then cast according to ASTM D638 [36] using high-density polyethylene (HDPE) molds as shown in Figure 8(a). For each test sample, six test specimens were fabricated with the sample geometry of 165 mm long, 3.2 mm thick, 13 mm width (Figure 8(b)). After pouring, the mixture remained at ambient temperature for 1 day and subsequently cured inside an oven at 121 ^{o}C (250 ^{o}F) for 2 h and post cured at ambient temperature for 6 more days. To fabricate the nanocomposites with brittle epoxy, the same procedure described above was used except that the samples were not degassed. Since the brittle epoxy has a high value of viscosity, degassing caused considerable foam in the vacuum oven. Skipping this stage, the mixture was mechanically mixed with the hardener (with 100:70 ratio) for 3-5 min just after 2 h of ultrasonication. The same molding and curing processes described above were applied for also brittle epoxy composites.



(a) (b)

Figure 8: (a) Tensile test specimen molds, (b) dimensions of the test specimens

4.1.3. Experimental Test and Results

The tests were performed in a 22-kips MTS servo hydraulic machine with a crosshead speed of 5 mm/min. The applied loads were recorded using the MTS data acquisition system, and displacements were captured by a laser extensometer attached to the system over a 50 mm gauge length at the middle portion of each specimen. Data sampling rate was 100 Hz. Figure 9 shows the test setup with one of the specimens.

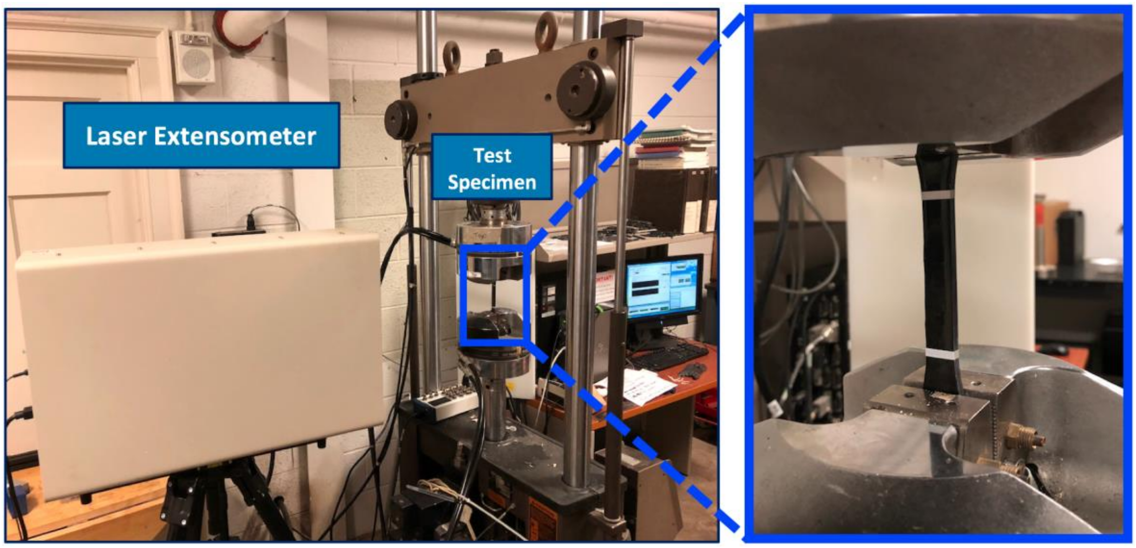
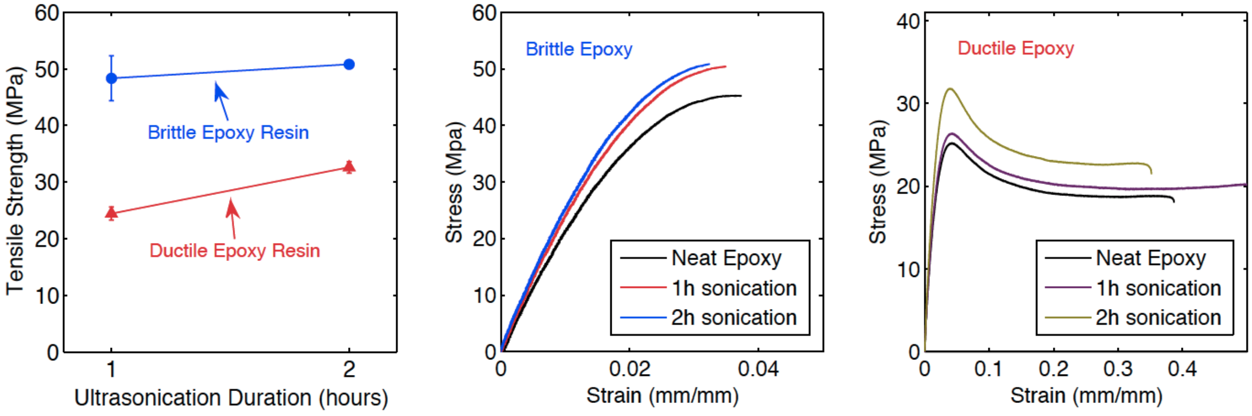


Figure 9: Test setup

Figure 10(a) compares the mean tensile strength of GNP-epoxy nanocomposites for two different epoxy resins ultrasonicated for 1 hour and 2 hours. An increase in the tensile strength for both epoxy resins was observed when the ultrasonication time was increased from 1 h to 2 h. Moreover, Figures 10(b) and 10(c) illustrate typical stress-strain curves for both epoxy resins without GNPs (neat epoxy) and with 0.25 wt.% GNPs (ultrasonicated 1 h or 2 h).

Since both optical images and tensile test results suggest a better dispersion with 2 hours ultrasonication, an ultrasonication time of 2 hours was used to prepare GNP-epoxy nanocomposites with different nanofiller ratios which is discussed later in this research.



(a) **(b)** **(c)**

Figure 10: (a) Mean tensile strength of GNP-epoxy nanocomposites for 1 hour and 2 hours of ultrasonication; tensile stress-strain curves for (b) brittle and (c) ductile epoxy resins with and without (0.25%) GNPs

4.2. Dispersion of GNPs into Hardener

Since in the earlier studies, both epoxy resin and hardener have been used as the first component to mix the GNPs, the effect of dispersing GNPs into epoxy hardener first was analyzed in this study. Similar to the first part, GNPs were first dispersed into hardener and then epoxy resin was added to the system and mixed by hand for 3-5 min. For the fabrication of test specimens, 1.5 h of ultrasonication duration was applied with the same procedure. The specimens prepared by ultrasonication of resin first was named as “resin sonicated” and by ultrasonication of hardener first was named as “hardener sonicated”. Figures 11(a) and 11(b) show the tensile stress-strain curves for brittle and ductile epoxies, respectively. In each figure, the results are shown for the neat epoxy and GNP/epoxy nanocomposites with 1 wt.% of GNPs and prepared through resin ultrasonication or hardener ultrasonication.

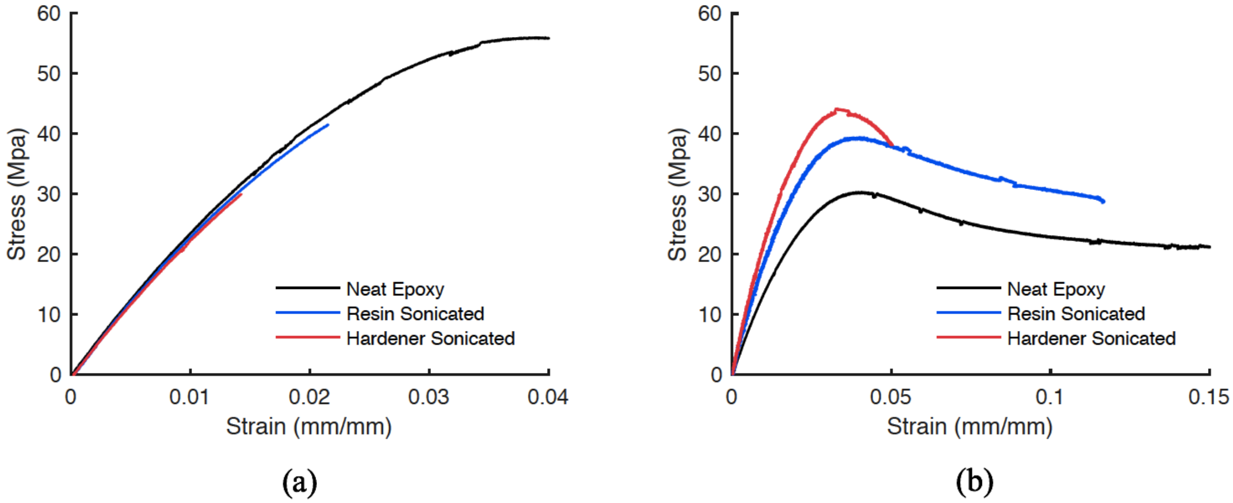


Figure 11: Stress-strain curves for (a) brittle epoxy: (b) ductile epoxy

For the brittle epoxy, the tensile strength of the neat epoxy was measured to be 56 MPa at a strain value of 4.0%. The addition of 1 wt.% GNPs decreased both tensile strength and failure elongation for both resin and hardener sonicated specimens. When the GNPs were first dispersed into the epoxy resin through sonication and then the hardener was added to the mixture, the tensile strength and failure strain of the specimens decreased to 41.5 MPa and 2.1%, respectively, as shown in Figure 11(a). For the hardener sonicated method, the reduction in tensile properties were even larger. In particular, the maximum stress was measured as 30 MPa and the strain at fracture was measured as 1.4%.

For the ductile epoxy, the maximum stress of the neat epoxy was measured to be 30.3 MPa with the failure strain of 15.0%. The tensile strength was observed to increase with both resin and hardener sonication methods compared to neat epoxy, while the failure elongations decreased. For resin sonicated GNP/epoxy nanocomposites with 1 wt.% GNPs, the maximum tensile stress increased to 39.3 MPa and the strain at fracture was 12.0%. For the specimen prepared with the hardener sonication process, the tensile strength further increased to 44.0 MPa, while the failure elongation reduced to 5.0%.

For brittle epoxy, hardener sonicated composites experienced significant decrease in both tensile strength and failure elongation. The results for resin sonicated specimens were observed to be better compared to hardener sonicated ones, however, there was a large decrease in tensile strength compared to neat epoxy. For ductile epoxy, on the other hand, the strength of the composite was increased 29.7 % as compared to neat epoxy. The strength was measured to be even higher for hardener sonicated method, but since the material lost a great deal of its flexibility, resin sonicated method was selected for further studies.

4.3. Dispersion of GNPs into Epoxy Matrix Using Ultrasonication and High Shear Mixing

In this section, the use of combined ultrasonicator and high shear mixer to disperse GNPs into epoxy matrix was studied. A total of nine different dispersion techniques was considered as shown in Table 4. In the first four methods, the GNPs were mixed into epoxy resin. The first two methods employed high shear mixing first, while in the other two methods the ultrasonication was first applied to GNP/epoxy mixture. The durations used for the ultrasonication and high shear mixing were either 30 minutes or 60 minutes. For the dispersion methods 1 and 2, first GNPs were added to the epoxy matrix, and then high shear mixing was applied at 3000 rpm for 30 min (for method 1) and 60 min (for method 2). Then 60 min and 30 min of ultrasonication was applied for method 1 and method 2, respectively. For methods 3 and 4, GNPs were dispersed into epoxy matrix using ultrasonication in the first place. 30 min of ultrasonication was applied first for method 3 which is then followed by 60 min of high shear mixing. The ultrasonication duration for method 4 was 60 min and afterwards 30 min of high shear mixing was applied. The total dispersion duration for each method was 1.5 hours and the hardener was added to the mixture and simply mixed by hand for 5 min before casting.

In the second four methods (5, 6, 7 and 8), the exact same procedure was applied except hardener used first to disperse GNPs. After dispersing GNPs into hardener, epoxy resin was added to the system and mixed by hand for 5 min and then poured to molds.

Table 4: Dispersion trials

No	***Dispersion Method***				
1	High Shear Mixer (30 min) ***(GNP + resin)***	+	Ultrasonication (60 min) ***(GNP + resin)***	+	Remove bubbles + Add hardener and mix by hand for 5 min
2	High Shear Mixer (60 min) ***(GNP + resin)***	+	Ultrasonication (30 min) ***(GNP + resin)***		
3	Ultrasonication (30 min) ***(GNP + resin)***	+	High Shear Mixer (60 min) ***(GNP + resin)***		
4	Ultrasonication (60 min) ***(GNP + resin)***	+	High Shear Mixer (30 min) ***(GNP + resin)***		
5	High Shear Mixer (30 min) ***(GNP + hardener)***	+	Ultrasonication (60 min) ***(GNP + hardener)***	+	Remove bubbles + Add hardener and mix by hand for 5 min
6	High Shear Mixer (60 min) ***(GNP + hardener)***	+	Ultrasonication (30 min) ***(GNP + hardener)***		
7	Ultrasonication (30 min) ***(GNP + hardener)***	+	High Shear Mixer (60 min) ***(GNP + hardener)***		
8	Ultrasonication (60 min) ***(GNP + hardener)***	+	High Shear Mixer (30 min) ***(GNP + hardener)***		
9	Ultrasonication (30 min) ***(GNP + acetone)***	+	High Shear Mixer (30 min) ***(GNP + acetone+ resin)***	+	Remove acetone and bubbles + Add hardener and mix by hand for 5 min

In the last dispersion method (method 9), acetone was used first to disperse GNPs since it was used for dispersion in the recent literature. GNPs were first dispersed in acetone by ultrasonication for 30 min at an amplitude of 40 % in an ice bath. Then epoxy resin was added to GNP/acetone mixture and sonicated for another 30 min. The mixture was the put inside the vacuum oven for 20 min at 80 ^{o}C and 29” Hg pressure and then rested for 1 day inside the oven at 80 ^{o}C (no vacuum) for complete removal of acetone. After the removal of acetone, hardener was added to the mixture and the test specimens were fabricated as explained above. For all the methods, 1 wt.% of GNPs were used in epoxy resin.

For the GNP/epoxy specimens prepared by the dispersion techniques described above, tensile tests were conducted to explore which dispersion method provides the best mechanical behavior. Only ductile epoxy used for this part of study. Figure 12 represents the tensile test results of the specimens.

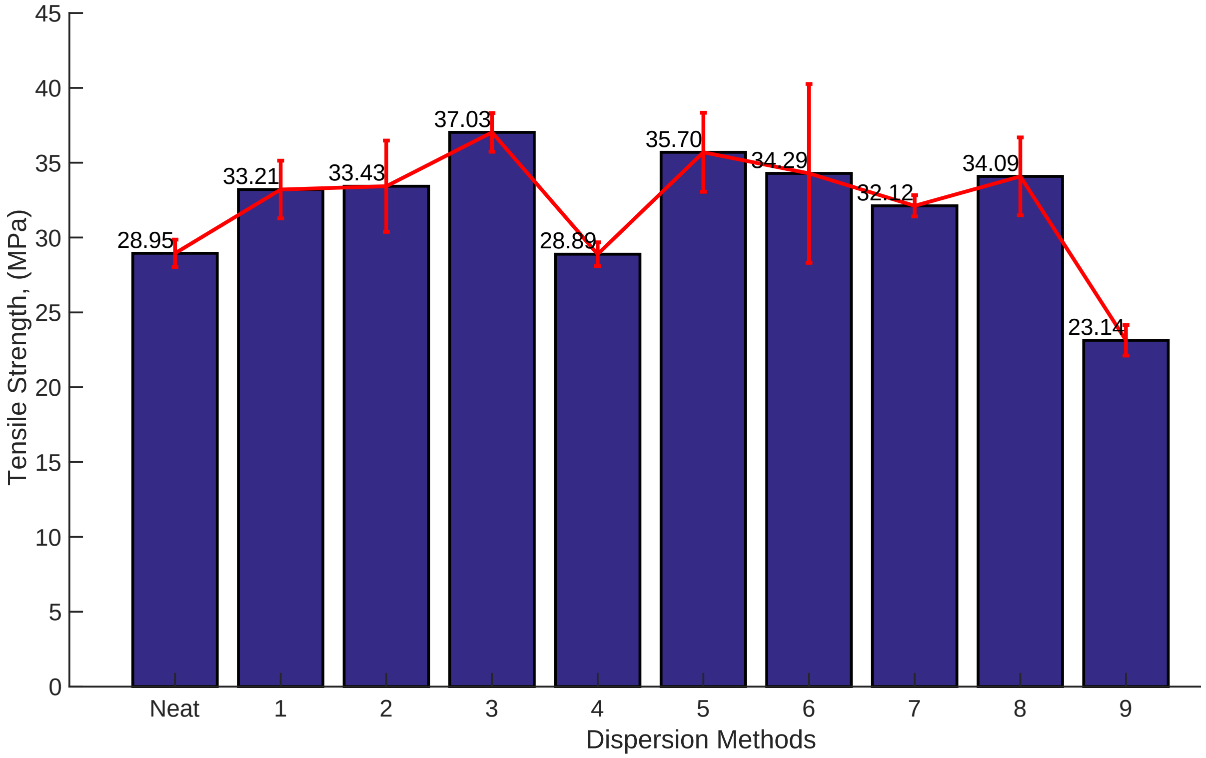


Figure 12: Tensile test results for dispersion methods

The tensile strength of neat epoxy was observed to be 28.95 MPa. The addition of GNPs with different dispersion techniques resulted in mostly in an increase in tensile strength as compared to neat epoxy. For the specimens fabricated with dispersion method 9 where acetone was used for dispersion, the tensile strength was observed to be 23.14 MPa which corresponds to 20% decrease compared to neat epoxy. In addition, the tensile strength of the GNP/epoxy composites prepared by the dispersion method 4 (28.95 MPa) almost same as that of the neat epoxy.

The tensile strength of GNP/epoxy composites increased in all other dispersion methods. This increase ranged between 13% observed for method 7 and 28% observed for method 3. The average tensile strength for method 3 specimens was observed to be 37.03 MPa. Since the largest tensile strength was achieved in the specimens fabricated by method 3, which is 30 min of ultrasonication followed by 60 min of high shear mixing, this method was selected for further studies in the next chapter.

4.4. Summary

An optimum dispersion technique was investigated in this chapter to fabricate GNP/epoxy nanocomposites. First, the use of ultrasonication alone was studied for the dispersion of GNPs into epoxy resin. The dispersion of GNPs first into hardener was also studied. The results indicated that the ultrasonication duration over 1 h can provide better dispersion. Then, several methods where the ultrasonication and high shear mixing were used together was studied. The results showed that 30 min ultrasonication followed by 60 min high shear mixing provides the largest increase in tensile strength. Based on the findings of this section, three dispersion techniques were selected to study the effect of GNP content on the tensile response of GNP/epoxy nanocomposites as discussed in detail in the next section.

5. EFFECT OF GNP CONCENTRATION ON TENSILE BEHAVIOR OF GNP/EPOXY NANOCOMPOSITES

Based on the results from previous section, tensile behavior of various concentrations of GNP/epoxy nanocomposites were studied in this section. Tensile tests were conducted for the specimens fabricated by;

- Ultrasonication alone (2 h and 1.5 h)
- 30 min of ultrasonication followed by 60 min of high shear mixing

5.1. Tensile Results for the Composites Fabricated by Ultrasonication Alone

The study of dispersion technique has showed that more than 1 hour of ultrasonication was needed for a good dispersion. It was also observed from the optical microscope images that there is a slight difference in particle size of GNPs for 1 h and 2 h of ultrasonication. Therefore, test specimens were fabricated by 2 hours of ultrasonication first, and then 1.5 h of ultrasonication were also used to fabricate test specimens. The fabrication process of specimens was exactly same as described in section 4.1.2.

5.1.1. Tensile Results of Composites Fabricated by 2 h of Ultrasonication

The change in the tensile behavior with various concentrations of GNPs were studied for both brittle epoxy and ductile epoxy. Figure 13 represents the stress-strain diagrams for increasing GNP contents for brittle epoxy. The ultimate tensile strength and maximum strain at fracture for neat epoxy was measured to be 44.2 MPa and 4.57%, respectively. Addition of 0.25% GNP into epoxy was increased the tensile strength to 50.8 MPa and maximum strain value to 4.60%. This indicate a 15% increase in tensile strength compared to neat epoxy.

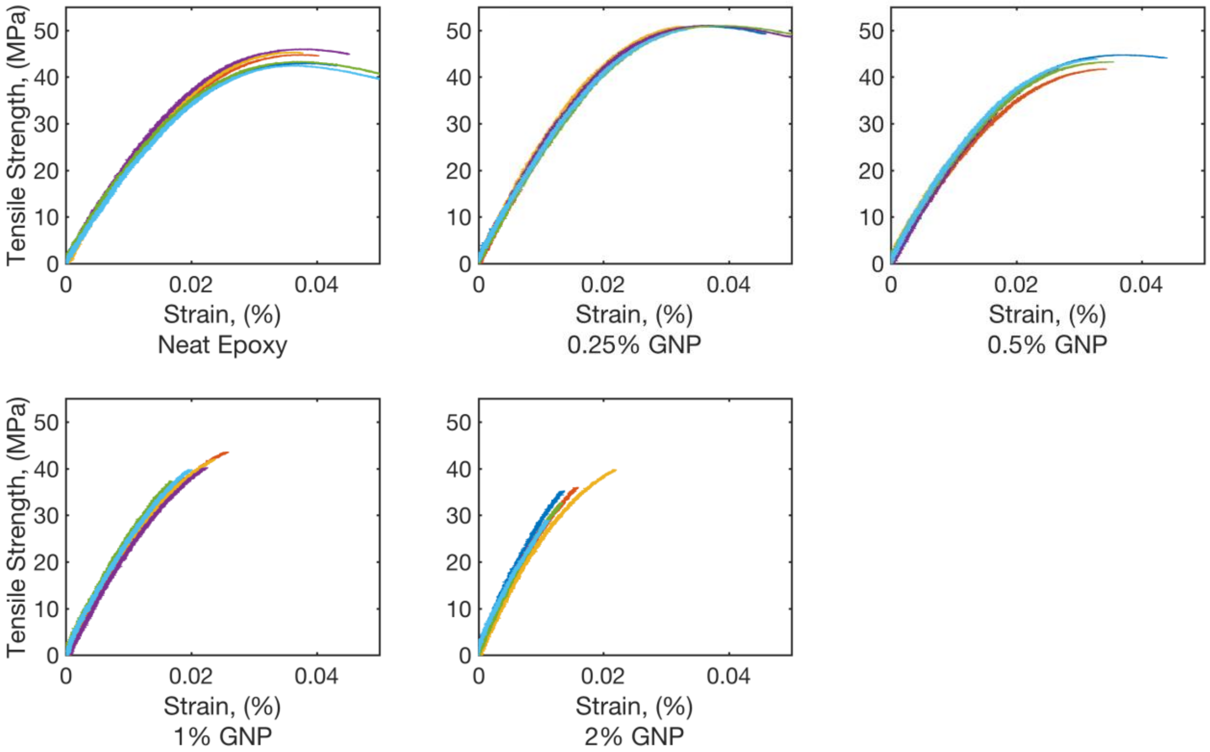


Figure 13: Stress-strain diagrams for GNP/brittle epoxy composites fabricated by 2 h ultrasonication

Over a concentration ratio of 0.25% by wt., the addition of more GNPs resulted in a decrease in tensile behavior. Both ultimate tensile strength and maximum strain at fracture were observed to decrease as compared to neat epoxy. Figure 14 shows the average tensile strength and ultimate strain values of composites at different GNP concentrations. For 0.5% GNP, no significant decrease was observed in tensile strength (43.1 MPa) but there was a considerable decrease in maximum strain (from 4.57% of neat epoxy to 3.44%). The ultimate tensile strength decreased to 40.2 MPa for the formulation containing 1 wt.% GNP in brittle epoxy. The decrease was measured to be the most for the composites having 2 wt.% of GNP. In particular, the tensile strength (33.6 MPa) decreased by 24% and the strain at fracture (1.48%.) decreased by 68%.

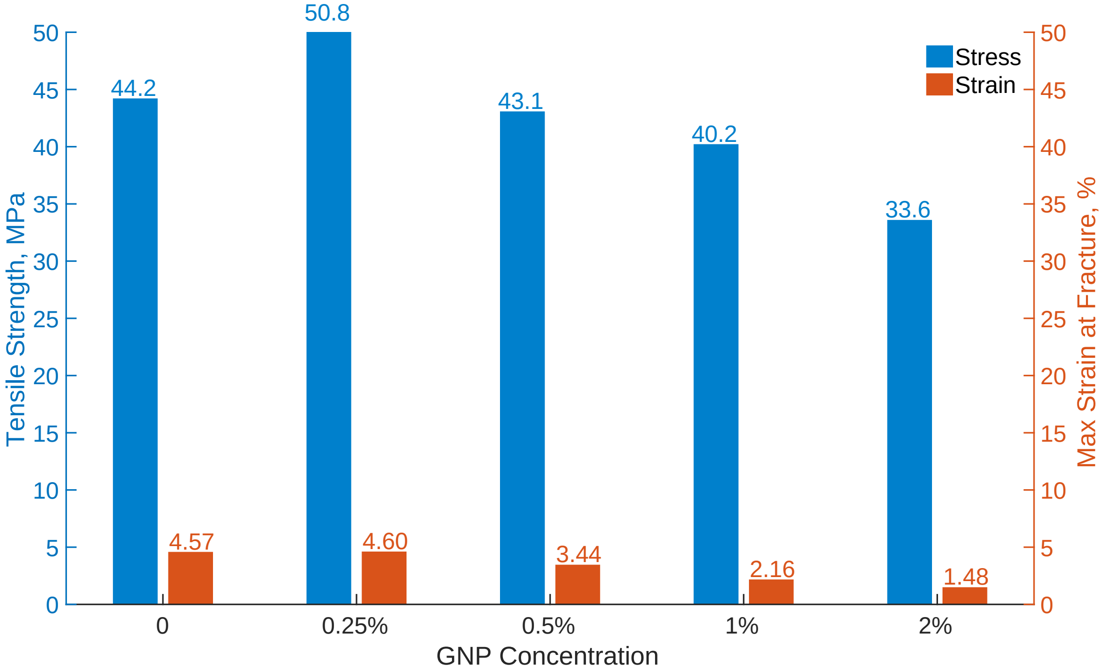


Figure 14: The variation of tensile strength and fracture strain of GNP/brittle epoxy composites fabricated by 2 h ultrasonication

Figure 15 shows the stress-strain diagrams for GNP/epoxy composites produced with ductile epoxy. Unlike brittle epoxy, an increase in GNP concentration resulted in an increase in tensile strength up to 1% GNP concentration. However, a decrease in fracture strain was observed with increasing GNP concentration. The ultimate tensile strength and fracture strain for neat ductile epoxy was measured as 26.3 MPa and 37.5%, respectively. Figure 16 shows the stress-strain curves for ductile epoxy with increasing GNP contents.

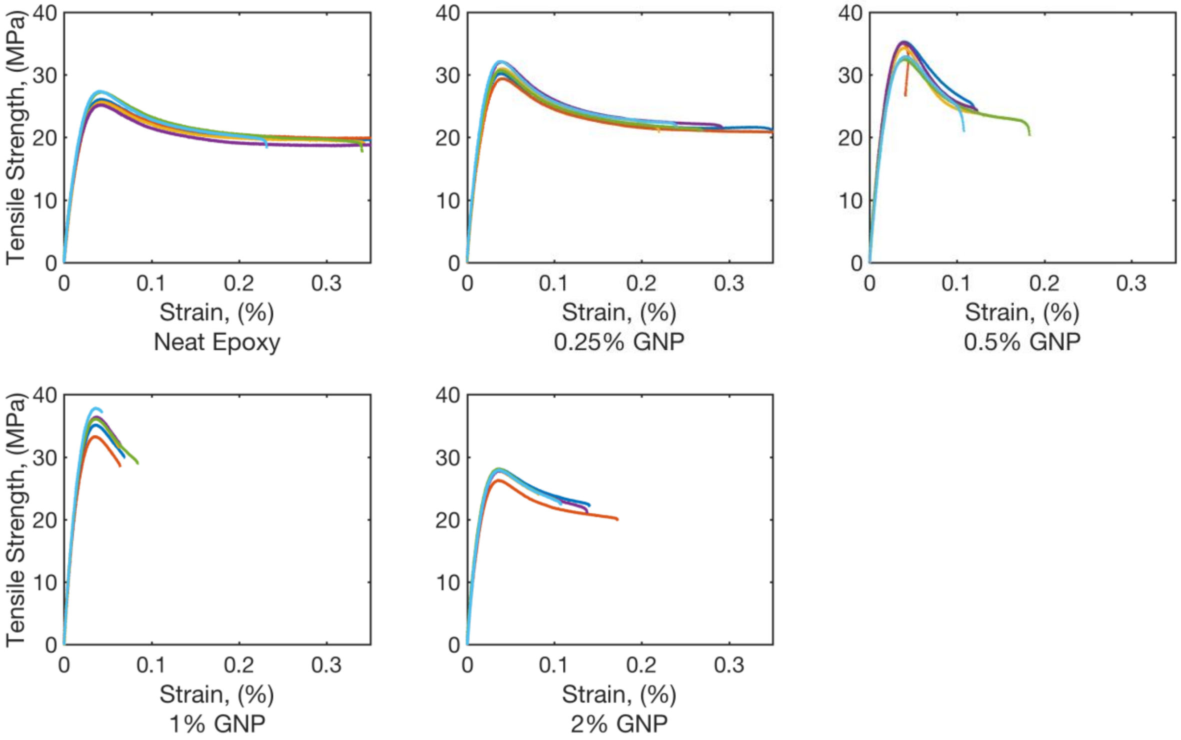


Figure 15: Stress-strain diagrams for GNP/ductile epoxy composites fabricated by 2 h ultrasonication

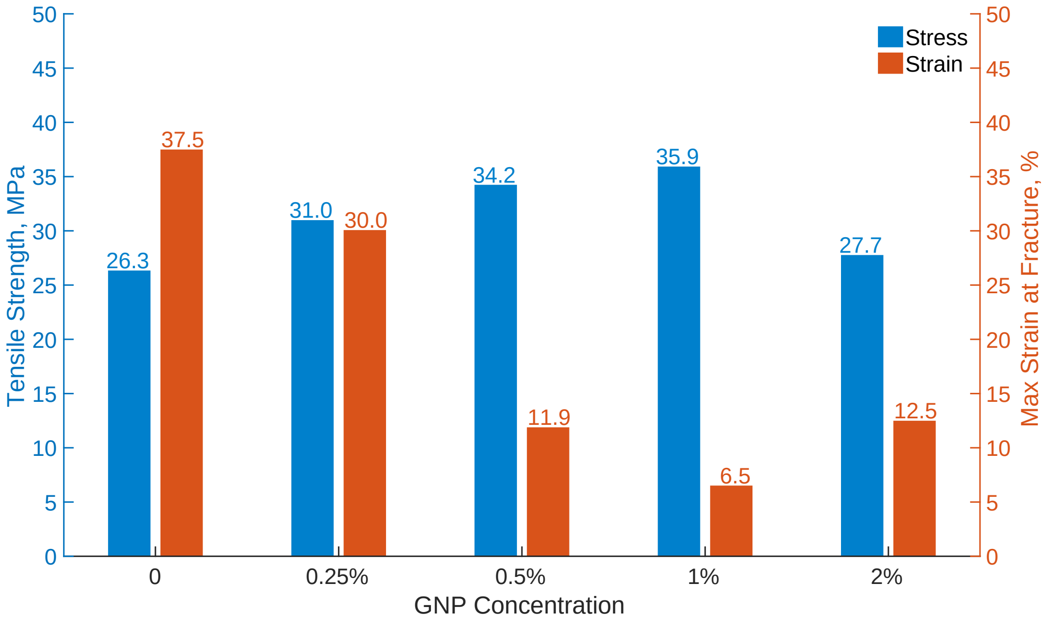


Figure 16: The variation of tensile strength and fracture strain of GNP/ductile epoxy composites fabricated by 2 h ultrasonication

The ultimate tensile strength increased to 35.9 MPa for the formulation containing 1wt.% of GNP. This indicates 36% increase in tensile strength of the GNP/epoxy composite compared to neat ductile epoxy. The specimens containing 1 wt.% of GNP fractured at an average strain of 6.5% which indicates 83% decrease in maximum strain compared to neat epoxy. Increasing GNP content to 2wt. did not further improved the tensile strength. In particular, the tensile strength was 27.7 MPa and fracture elongation was 12.5% for the specimens with 2% GNPs.

Tensile modulus of brittle and ductile epoxy composites was also computed. The modulus for the GNP/epoxy composite fabricated from ductile epoxy increased from 0.63 GPa for neat epoxy to 1.06 GPa for the sample containing 1 wt.% GNP. Further increasing the GNP content (2 wt.%) caused decrease in modulus (0.75 GPa). The tensile modulus for the neat brittle epoxy was 1.20 GPa and the addition of GNPs at different concentrations did not significantly change the tensile modulus. Figure 17 illustrates the variation in tensile properties of both brittle and ductile epoxy with different GNP concentrations. Table 5 shows all the tensile results for the GNP/epoxy composites fabricated by 2 h ultrasonication.

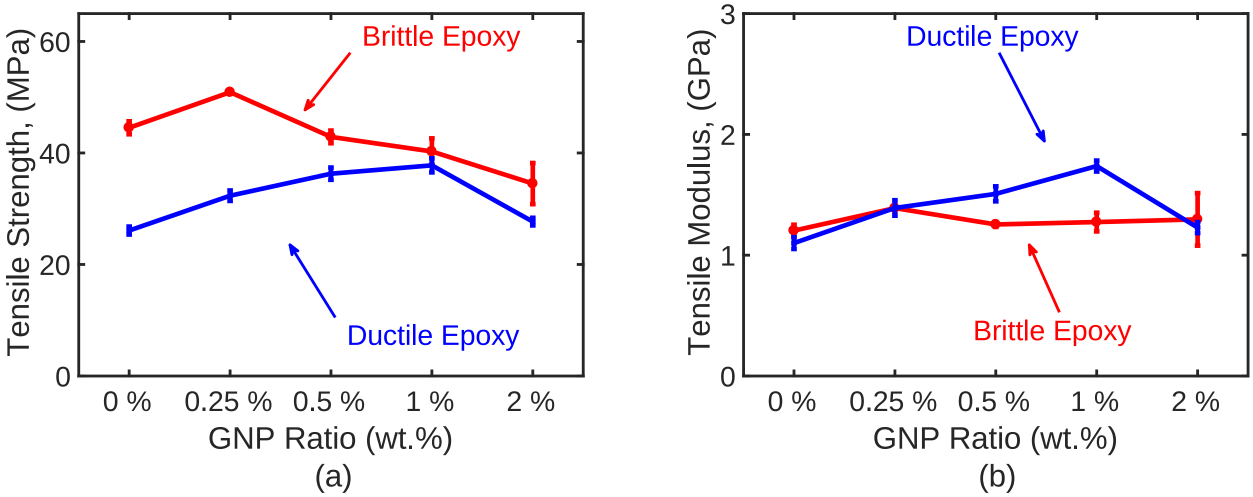


Figure 17: (a) Tensile strength and (b) tensile modulus for epoxy nanocomposites fabricated by 2 h ultrasonication with different GNP concentrations

Table 5: Tensile test results for composites fabricated by 2 h ultrasonication

Epoxy Type	GNP *(wt.%)*	Tensile Strength *(MPa)*	Tensile Modulus *(GPa)*	Strain at Fracture *(%)*
Brittle Epoxy	0	44.2 ± 1.16	1.20 ± 0.05	4.57 ± 0.6
	0.25	50.8 ± 0.24	1.39 ± 0.03	4.60 ± 1.4
	0.5	43.1 ± 1.13	1.25 ± 0.02	3.44 ± 0.7
	1	40.2 ± 2.35	1.27 ± 0.08	2.16 ± 0.6
	2	33.6 ± 3.69	1.30 ± 0.22	1.48 ± 0.6
Ductile Epoxy	0	26.3 ± 0.71	1.10 ± 0.05	37.5 ± 6.9
	0.25	31.0 ± 0.93	1.39 ± 0.06	30.0 ± 7.2
	0.5	34.2 ± 1.10	1.51 ± 0.06	11.9 ± 4.4
	1	35.9 ± 1.26	1.74 ± 0.04	6.5 ± 0.8
	2	27.7 ± 0.68	1.23 ± 0.04	12.5 ± 3.1

5.1.2. Tensile Results of Composites Fabricated by 1.5 h of Ultrasonication

Additional GNP/epoxy composite specimens were prepared by applying 1.5 h of ultrasonication to disperse GNPs into epoxy resin. Both brittle and ductile epoxy matrices were used for the composite fabrication. The same GNP concentrations discussed in earlier section were used to observe the difference in tensile behavior. Figure 18 shows the stress strain diagrams of composites fabricated by brittle epoxy using 1.5 h ultrasonication and Figure 19 shows the mean stress and strain values. The tensile strength of neat epoxy was measured as 46.5 MPa and strain at fracture was measured as 5.01%. Similar to the brittle epoxy composites fabricated by 2 h of ultrasonication, an increase was observed in tensile strength for the formulation containing 0.25% GNP. In particular, the tensile strength and strain at fracture values was measured as 50 MPa and

4.55%, respectively. After this ratio, further increasing GNP content did not considerably affect the tensile strength. The tensile strength had its lowest value for the composites containing 1% GNP as 38.5 MPa and the maximum fracture strain was found to be the lowest for 0.5% GNP/epoxy composites (2.96%).

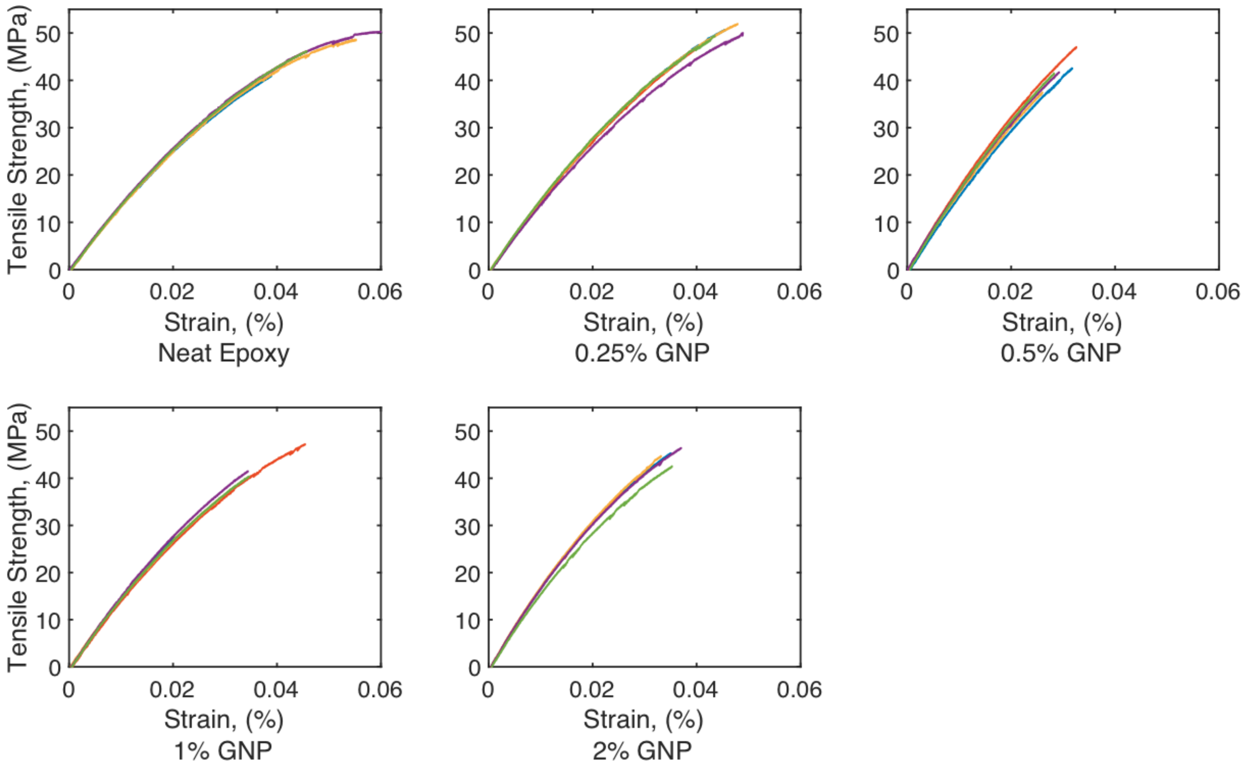


Figure 18: Stress-strain diagrams for GNP/brittle epoxy composites fabricated by 1.5 h ultrasonication

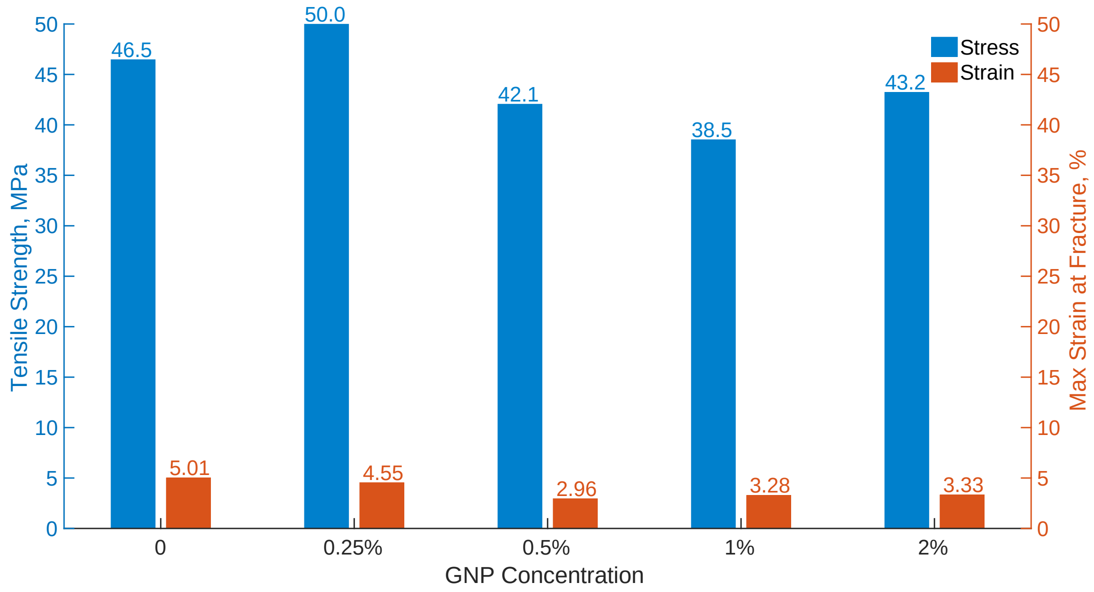


Figure 19: The variation of tensile strength and fracture strain of GNP/brittle epoxy composites fabricated by 1.5 h ultrasonication

Figure 20 shows the stress-strain diagrams of ductile epoxy composites fabricated by 1.5 h ultrasonication. The tensile strength of neat epoxy was measured as 26.9 MPa with 20.9% fracture strain. Addition of 0.25% of GNPs showed almost no effect in tensile strength but the strain at fracture increased from 20.9% for neat epoxy to 24.2%. Further addition of GNPs from this point caused a decrease in maximum strain values having the lowest value (11.4%) for 1% GNP concentration. On the other hand, the composites having 1% GNPs showed the maximum tensile strength with a value 36.5 MPa as shown in Figure 21. This indicate 36% increase compared to neat epoxy.

Figure 22 shows tensile modulus and tensile strength variation with increasing GNP concentrations for both brittle epoxy and ductile epoxy. Similar to 2 h of ultrasonication, tensile modulus for ductile epoxy composites increased with the addition of GNP up to 1% concentration. The modulus increased from 1.2 GPa for neat epoxy to 1.67 GPa for the sample containing 1 wt. % of GNP after which a slight decrease observed. For the brittle epoxy, the tensile modulus increased from 1.42 GPa for neat epoxy to 1.72 GPa by increasing the GNP concentration to 0.5%.

Further increasing GNP content to 1% first caused a decrease (1.51 GPa) and then an increase for 2wt.% formulation (1.69 GPa). The highest increase in tensile modulus for brittle and ductile epoxy composites were 39% for ductile epoxy (for 1% GNP) and 21% for brittle epoxy (for 0.5% GNP).

Table 6 shows all the tensile test results for composites fabricated by 1.5 h ultrasonication.

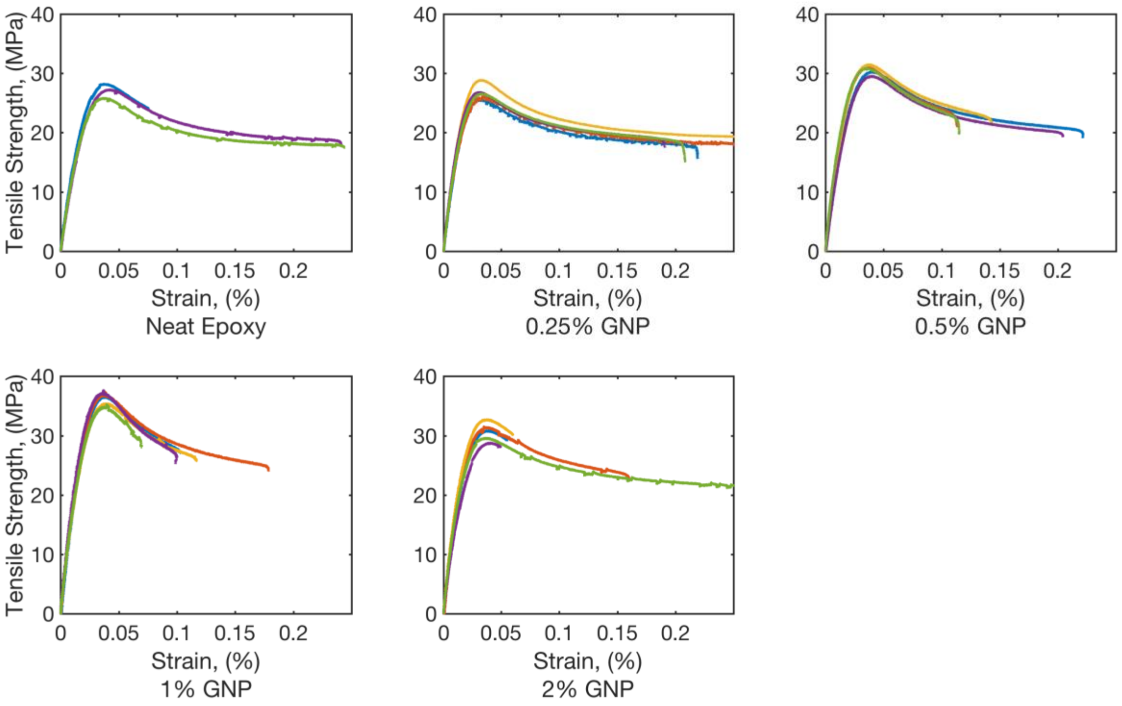


Figure 20: Stress-strain diagrams for GNP/ductile epoxy composites fabricated by 1.5 h ultrasonication

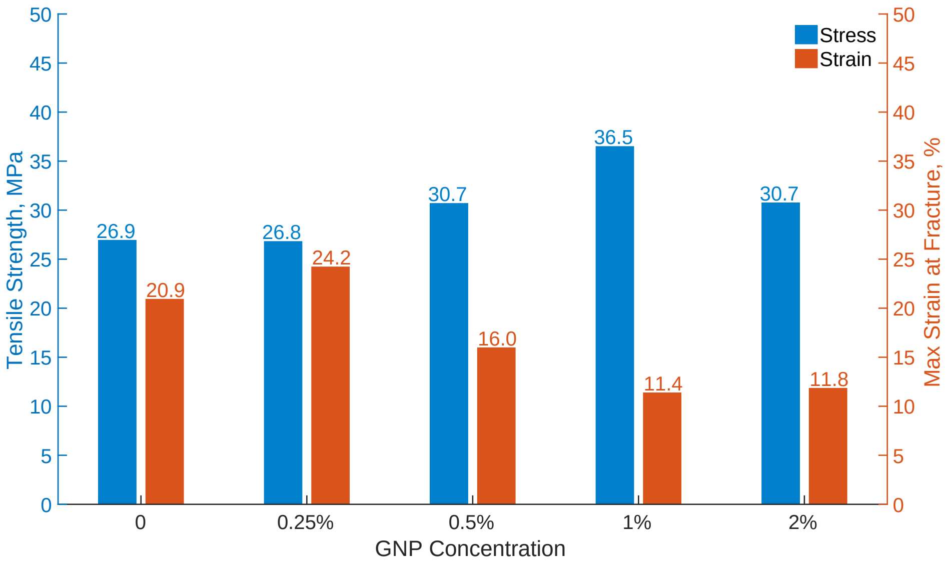


Figure 21: The variation of tensile strength and fracture strain of GNP/ductile epoxy composites fabricated by 1.5 h ultrasonication

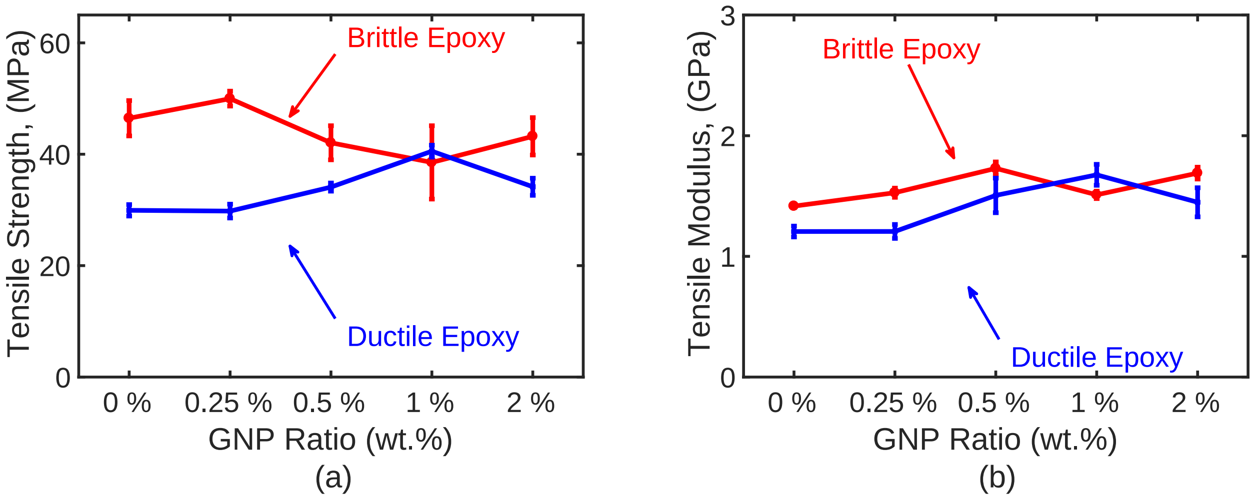


Figure 22: (a) Tensile strength and (b) tensile modulus for epoxy nanocomposites fabricated by 1.5 h ultrasonication with different GNP concentrations

Table 6: Tensile test results for composites fabricated by 1.5 h ultrasonication

Epoxy Type	GNP *(wt.%)*	Tensile Strength *(MPa)*	Tensile Modulus *(GPa)*	Strain at Fracture *(%)*
Brittle Epoxy	0	46.5 ± 3.18	1.42 ± 0.01	5.01 ± 0.91
	0.25	50.0 ± 1.34	1.53 ± 0.04	4.55 ± 0.26
	0.5	42.1 ± 3.06	1.73 ± 0.05	2.96 ± 0.24
	1	38.5 ± 6.58	1.51 ± 0.03	3.28 ± 0.83
	2	43.2 ± 3.36	1.69 ± 0.05	3.33 ± 0.39
Ductile Epoxy	0	26.9 ± 1.02	1.21 ± 0.04	20.9 ± 6.9
	0.25	26.8 ± 1.24	1.21 ± 0.06	24.2 ± 7.2
	0.5	30.7 ± 0.72	1.50 ± 0.14	16.0 ± 4.4
	1	36.5 ± 1.07	1.68 ± 0.09	11.4 ± 0.8
	2	30.7 ± 1.53	1.45 ± 0.12	11.8 ± 3.1

5.2. Tensile Results of Composites Fabricated by Combination of Ultrasonication and High Shear Mixing

In this section, the tensile test results on GNP/epoxy composites fabricated by a dispersion method that employs both ultrasonication and high shear mixing was studied. Only ductile epoxy was considered in this section. Figure 23 shows the stress-strain diagrams of the tested specimens with different GNP concentrations and Figure 24 shows the variation in tensile properties of the GNP/epoxy specimens fabricated by 30 min ultrasonication and 60 min high shear mixing.

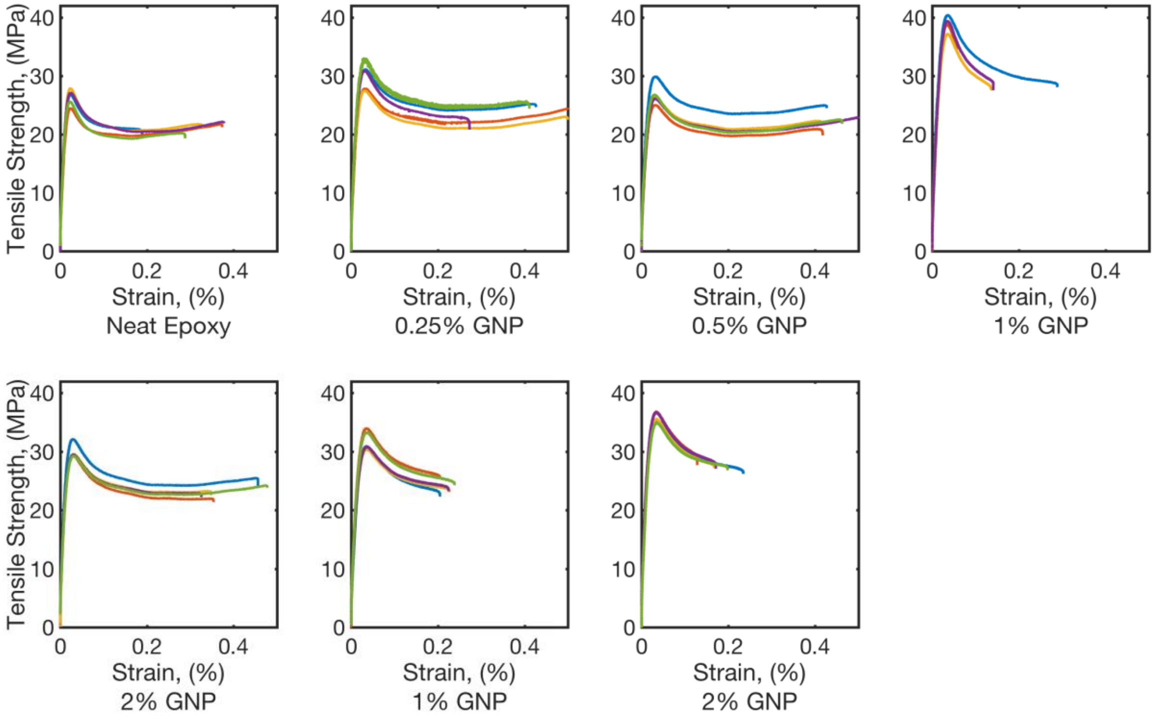


Figure 23: Stress-strain diagrams for GNP/brittle epoxy composites fabricated by 30 min ultrasonication and 60 min high shear mixing

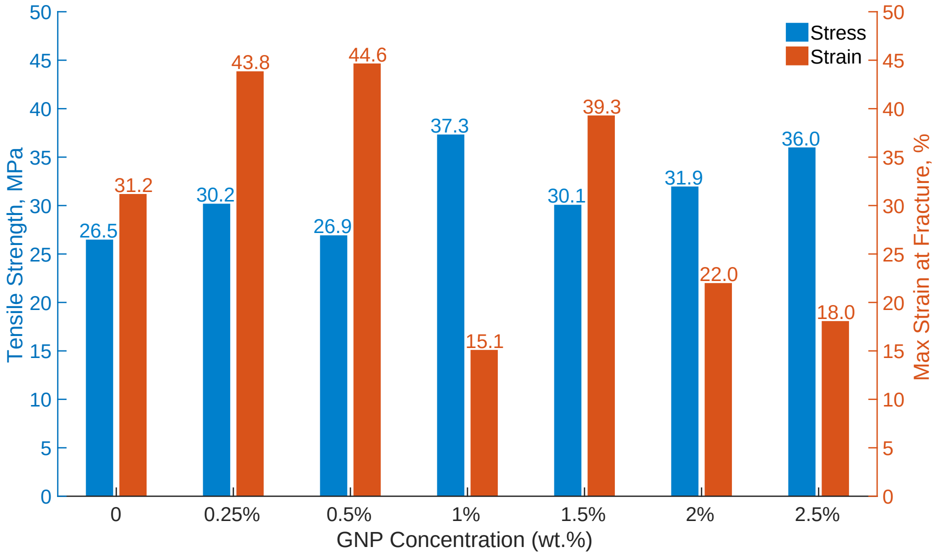


Figure 24: The variation of tensile strength and fracture strain of GNP/ductile epoxy composites fabricated by 30 min ultrasonication and 60 min high shear mixing

The tensile strength of the specimens fabricated with this dispersion method initially increased with the addition of 0.25% of GNPs (30.2 MPa) compared to neat epoxy (26.5 MPa) but then remained almost unchanged for 0.5% GNP (26.9 MPa) addition. The largest tensile strength value was observed as 37.3 MPa for the composite containing 1% GNPs. After 1% GNP content, there was a decrease in the tensile strength for the formulation of 1.5% GNPs (30.1 MPa) and 2% GNPs (31.9 MPa) compared to the specimens with 1% GNPs. For the formulation of 2.5% the tensile strength was measured to be 36 MPa. It should be noted that for all GNP concentrations, there was an increase in the tensile strength when the specimens were prepared with this dispersion technique. The strain at fracture values considerably increased for the specimens with 0.25% and 0.5% GNPs compared to neat epoxy. The smallest value of fracture strain was measured for 1% of GNPs. Figure 25 illustrates the variation of tensile strength and tensile modulus with GNP content. The tensile modulus values were observed to decrease for 0.5% (1.41 GPa) and 2% 1.34 GPa) of GNPs as compared to neat epoxy (1.46 GPa). For other GNP concentrations, the modulus increased compared to neat epoxy having the highest value as 1.62 GPa for the formulation of 1% GNPs in ductile epoxy. Table 7 shows all the tensile results for composites fabricated by 30 min ultrasonication continued by 60 min high shear mixing.

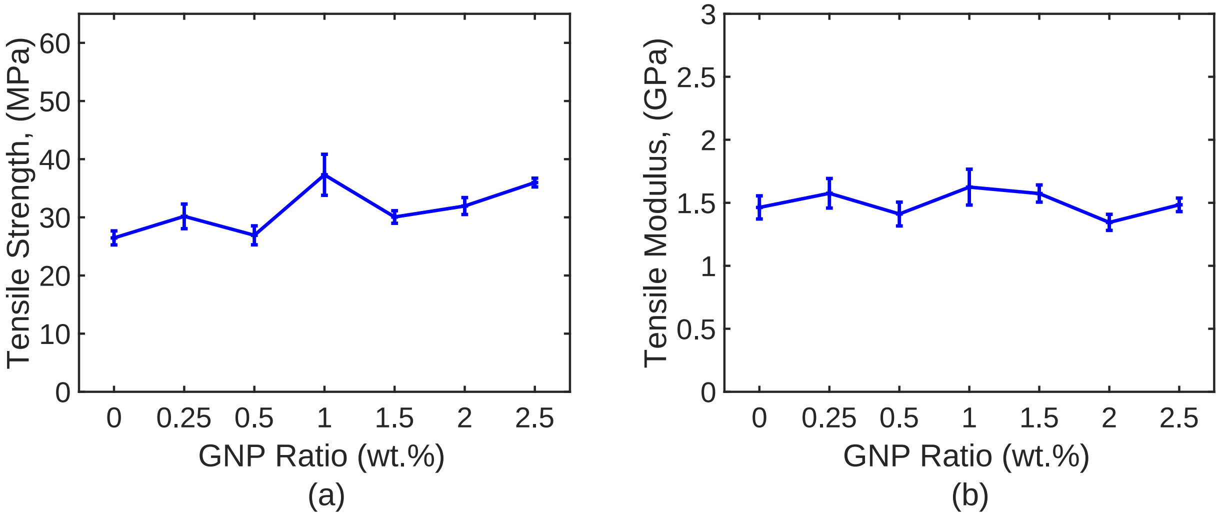


Figure 25: (a) Tensile strength and (b) tensile modulus for ductile epoxy nanocomposites fabricated by 30 min of ultrasonication and 60 min high shear mixing with different GNP concentrations

Table 7: Tensile test results for composites fabricated by 30 min ultrasonication and 60 min high shear mixing

Epoxy Type	GNP *(wt.%)*	Tensile Strength *(MPa)*	Tensile Modulus *(GPa)*	Strain at Fracture *(%)*
Ductile Epoxy	0	26.5 ± 1.04	1.46 ± 0.05	31.2 ± 11.5
	0.25	30.2 ± 1.61	1.58 ± 0.07	43.8 ± 12.8
	0.5	26.9 ± 1.22	1.41 ± 0.05	44.6 ± 4.30
	1	37.3 ± 2.68	1.62 ± 0.11	15.1 ± 7.50
	1.5	30.1 ± 0.82	1.57 ± 0.04	39.3 ± 7.74
	2	31.9 ± 1.11	1.34 ± 0.05	22.0 ± 1.32
	2.5	36.0 ± 0.57	1.48± 0.04	18.0 ± 3.53

5.3. Microstructural Analysis

Figure 26 indicates the Scanning Electron Microscopy (SEM) image of GNP-epoxy nanocomposites fabricated by 2 h of ultrasonication with ductile epoxy resin and 0.5 wt. % of GNPs. The image was taken from the fracture surface of the composites and it can be seen that GNPs are generally well-dispersed in the epoxy matrix. The average particle size of the GNPs at fracture surface was 3-4 μm. Considering the average GNPs size of 25 μm, it can be interfered that the average GNP particle size reduced after 2 h of ultrasonication. Figure 27 also shows a similar dispersion characteristics from the brittle epoxy specimens with 0.25% of GNPs fabricated by 1.5 h of ultrasonication. Similar to the ductile one, the particle sizes for brittle epoxy composites was observed to be approximately 3-4 μm. This behavior suggests that at least 1.5 h of ultrasonication is needed for good dispersion.

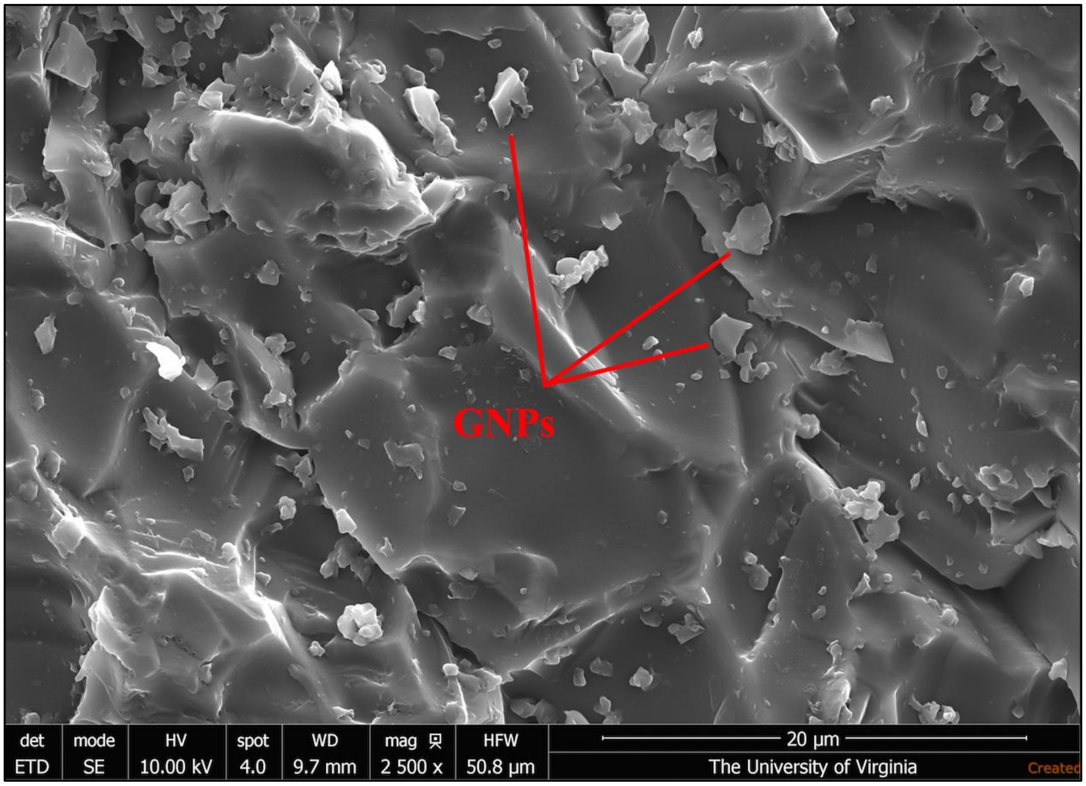


Figure 26: SEM image of the fracture surface of one specimen fabricated by 2 h of ultrasonication and containing 0.5% GNP in ductile epoxy

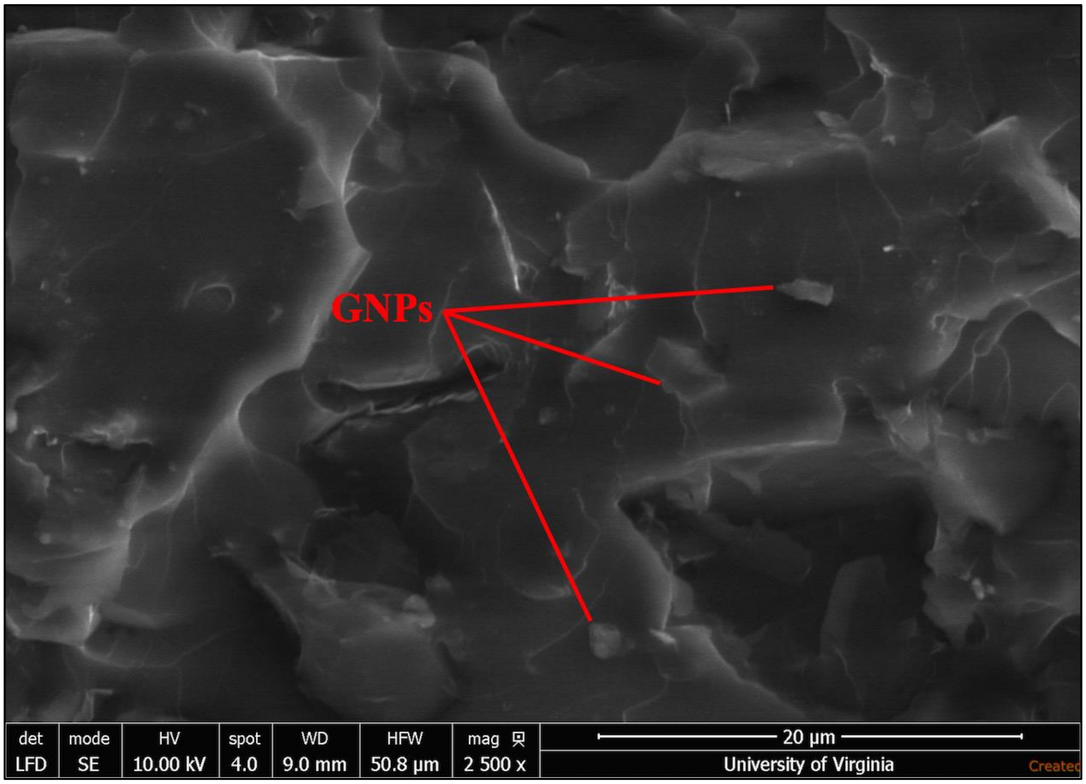


Figure 27: SEM image of the fracture surface of one specimen fabricated by 1.5 h of ultrasonication and containing 0.25% GNP in brittle epoxy

Increasing GNP content led to agglomeration in the microstructure. Further increase in. For example, Figure 28 shows an agglomerate in 1% GNP/ductile epoxy specimen. The size of GNPs agglomerates in this specimen was measured as around 5 μm containing GNPs of 2-4 μm in size. When the GNP content was over 1 wt. %, larger agglomerates were observed. Figure 29 represents a large agglomerate presents in 2% GNP ductile epoxy specimen fabricated by 30 min ultrasonication and 60 min high shear mixing. The size of the agglomerate was measured to be about 30 μm containing many small GNP particles. Note that it was observed in the tensile test results that GNP/epoxy specimens with GNP content over 1% experience a decrease in tensile strength and tensile modulus, which can be explained by the increasing amount and size of agglomerates inside the composite with increasing GNP content.

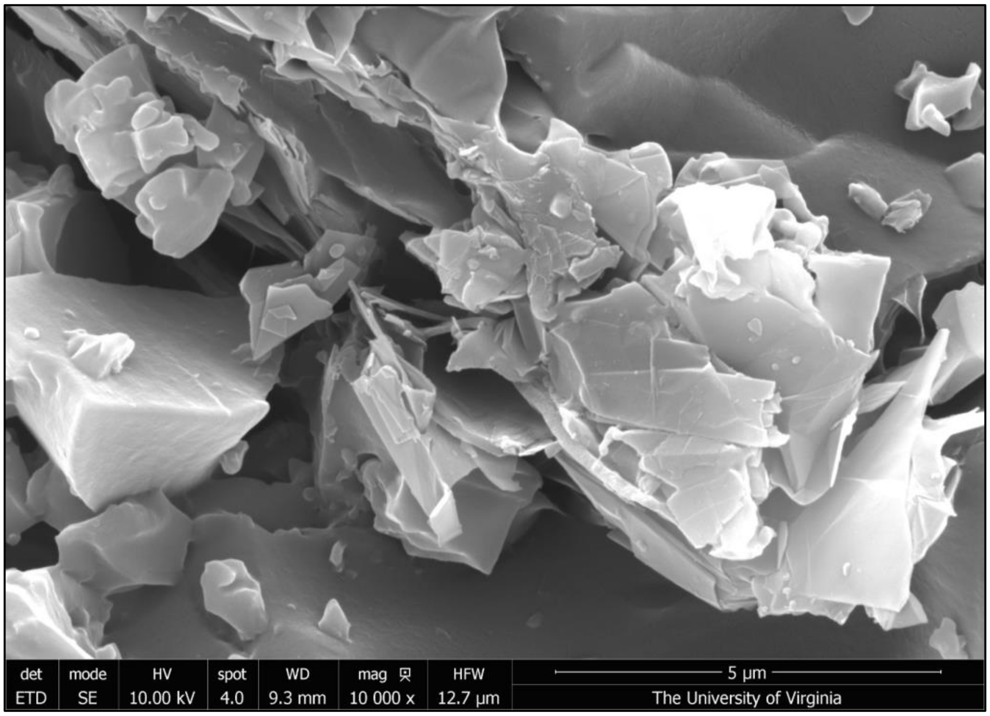


Figure 28: GNP agglomerates in 1% GNP ductile epoxy composite

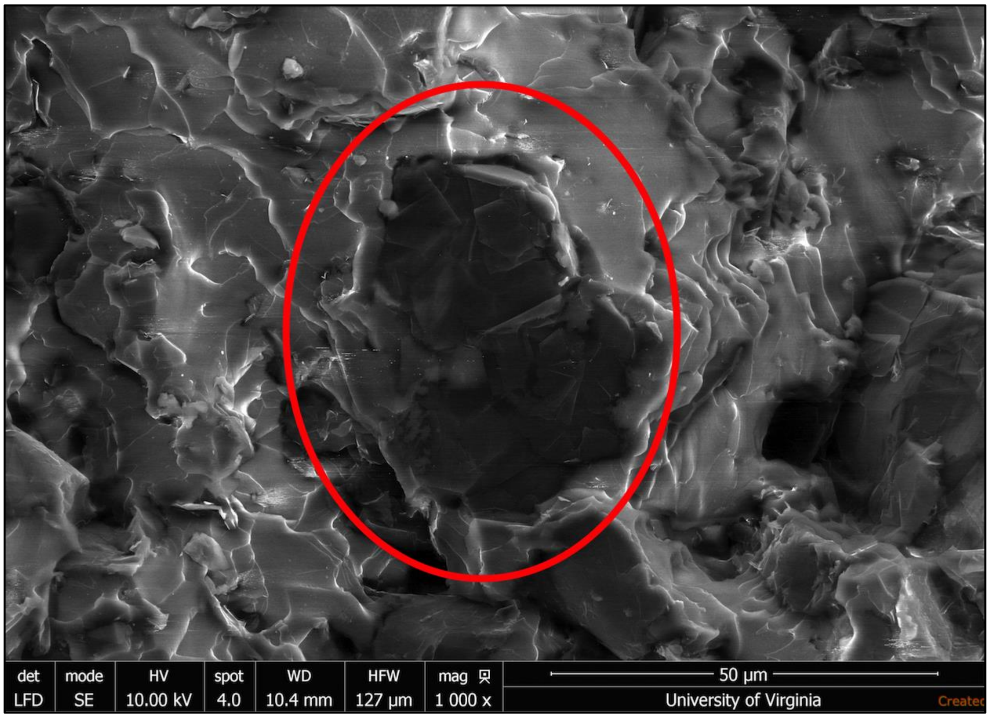


Figure 29: Large GNPs agglomeration in 2% GNP in ductile epoxy fabricated by 30 min ultrasonication and 60 min high shear mixing

5.4. Summary

Table 8 and Table 9 summarize the maximum tensile strength and tensile modulus improvements, respectively in both brittle and ductile epoxy resins achieved by addition of specific content of GNPs dispersed through different mixing techniques. For the brittle epoxy, the formulation containing 0.25% GNP showed the maximum improvement for the tensile strength compared to other GNP contents. When the GNPs were dispersed through 2 h of ultrasonication, there was 14.9% increase in tensile strength. The same specimens also exhibited 15.8% increase in tensile modulus compared to neat epoxy. However, the largest increase (21.6%) in tensile modulus for brittle epoxy was observed in the specimens with 0.5% GNPs.

The addition of GNPs into ductile epoxy resulted in larger improvements in tensile properties of the epoxy compared to those observed in GNP/brittle epoxy composites. For all techniques used to disperse GNPs into ductile epoxy, the highest increase in tensile strength and tensile modulus was observed for the specimens with 1% GNP content. For the specimens fabricated through 2 h ultrasonication, the tensile strength increased 36.5% with 1% GNP addition. Similarly, for the specimens fabricated with 1.5 h ultrasonication, 35.6% increase in tensile strength was present for 1% GNP formulation. The largest increase in tensile strength (40.7%) was observed for the specimens fabricated with the dispersion method that employed 30 min ultrasonication followed by 60 min high shear mixing. On the other hand, among three dispersion techniques, 2 h ultrasonication provided the highest increase (58.2%) in tensile modulus.

Since the reinforcement effects of GNPs was better in ductile epoxy, this epoxy was used in next section together with 1% GNP concentration to fabricate SMA fiber-GNP/epoxy composites.

Table 8: Tensile strength improvements compared to neat epoxies

	Brittle Epoxy		Ductile Epoxy	
	Improvement	Formulation	Improvement	Formulation
2h Ultrasonication	14.9 %	0.25% GNP	36.5 %	1% GNP
1.5 h Ultrasonication	7.5 %	0.25% GNP	35.6 %	1% GNP
30 min Ultrasonication + 60 min HSM	-	-	40.7 %	1% GNP

Table 9: Tensile modulus improvements compared to neat epoxies

	Brittle Epoxy		Ductile Epoxy	
	Improvement	Formulation	Improvement	Formulation
2h Ultrasonication	15.8 %	0.25% GNP	58.2 %	1% GNP
1.5 h Ultrasonication	21.8 %	0.5% GNP	38.8 %	1% GNP
30 min Ultrasonication + 60 min HSM	-	-	11.0 %	1% GNP

6. MECHANICAL CHARACTERIZATION OF SMA FIBER-GNP/EPOXY COMPOSITES

6.1. Fabrication of Test Specimens

SMA-GNP/epoxy coupons were fabricated using a vacuum assisted hand lay-up technique as guided by the ASTM D5687 [37] specifications. The cross section of the test specimen was 12.5×1 mm^2 as shown in Figure 30. On a metal plate, non-porous release film was first attached to isolate the specimen from the plate and peel ply was added over the release film to facilitate peeling of the specimen after curing.

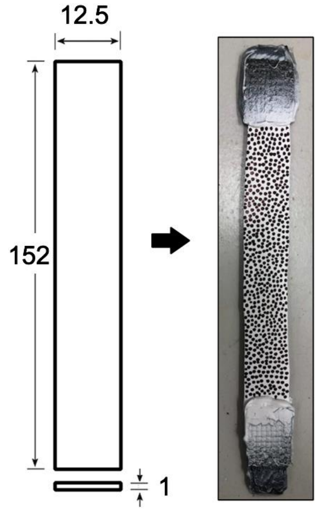


Figure 30: Test specimen dimensions (in mm)

Total of 84 SMA strands were placed on the peel ply and arranged in three layers with 28 strands in each layer. The test specimens were fabricated for a total fiber volume ratio of 50%. The strands were impregnated into epoxy resin and another peel ply was added. On the top of the peel ply, a porous release film and breather ply were applied to provide an air bath and facilitate absorbing the excess epoxy. The entire system was finally sealed using a nylon bag. A vacuum pump was connected (Figure 31 to the vacuum port in the nylon bad for 2 minutes to remove air bubbles and excess epoxies from the specimen. After 48 hours from fabrication, the specimen was removed from the system and was left to cure for another 5 days before being tested. Specimens were fabricated with SMA fibers and two epoxy resins: neat epoxy and GNP/epoxy composite. The ductile epoxy resin was used to fabricate SMA fiber reinforced composites. GNP/epoxy resin used in the fabrication contained 1 wt. % GNPs. GNPs were dispersed into ductile epoxy through 30 min ultrasonication and 60 min high shear mixing. Two specimens were fabricated for both SMA/epoxy and SMA-GNP/epoxy composites.

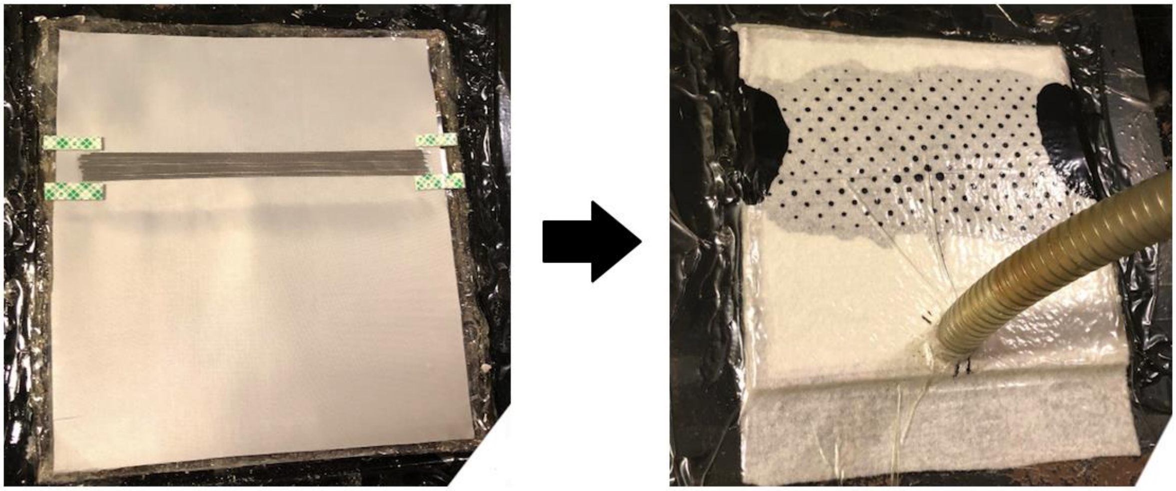


Figure 31: Vacuum assisted hand lay-up technique as guided by the ASTM D5687

6.2. Test Procedure and Setup

An experimental testing program was followed to investigate the mechanical behavior of the fabricated composites according to ASTM F2516 [38]. The tests were performed in a 22 kips MTS servo hydraulic machine with a loading protocol of first (1) loading with a crosshead speed of 1 mm/min until 6% strain and unloading; (2) loading again until rupture with a crosshead speed of 10 mm/min. Test loads were recorded using the MTS data acquisition system, and the displacements were captured by a laser extensometer attached to the system. Data sampling rate was 100 Hz. CFRP tabs were glued on both sides of the gripping area in each specimen to prevent crushing of this area by the grips of the load frame as shown in Figure 30.

Digital Image Correlation (DIC) was used during the experiments to monitor the strain evolution and deformation fields. DIC is a real-time, full-field and non-contact optical measurement system that utilizes a series of sequential images captured during loading to track and correlate patterns within a subset space. This can in turn be used to identify deformation behavior. To enable the DIC measurements, the surface of specimens needs to be textured with a random speckle pattern which was accomplished by painting the specimens to white and putting black dots on them. In this study, one DIC camera with 12-mm lens was used for DIC imaging. In addition to the DIC measurements, a single thermal camera was used to evaluate the temperature behavior of the specimens while loading. Figure 32 shows the test setup with one of the specimens.

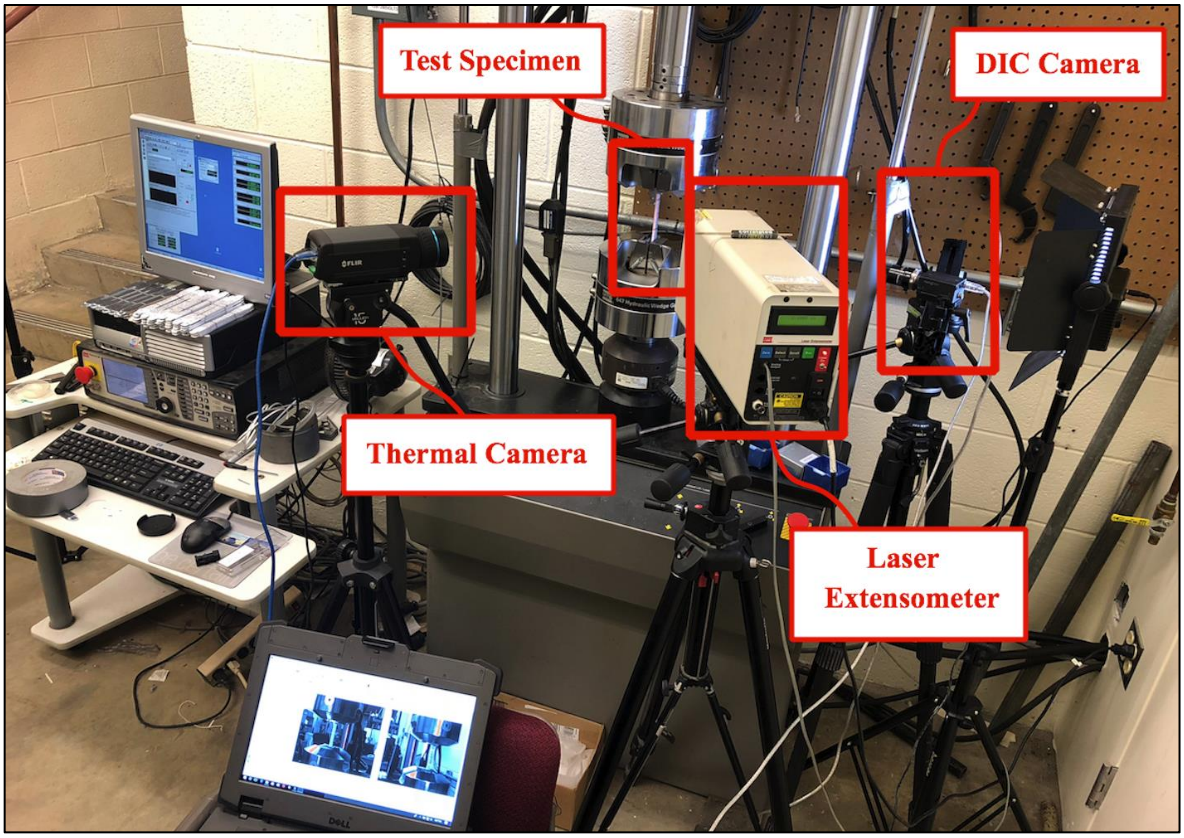


Figure 32: Test setup

6.3. Tensile Test Results

Figure 33 shows the tensile test results of one of the SMA/epoxy specimens. In the first loading cycle, the phase transformation start stress level of the composite was 372 MPa. The loading was continued until 6% strain and then specimen was unloaded with force control method. Upon unloading, 0.45% of residual strain was observed. Then the second loading cycle was applied and the phase transformation start stress level in this loading cycle was measured as 359 MPa. The loading continued in a monotonic manner until rapture and the tensile strength of the specimen was measured as 555 MPa with 12.9 % of fracture strain.

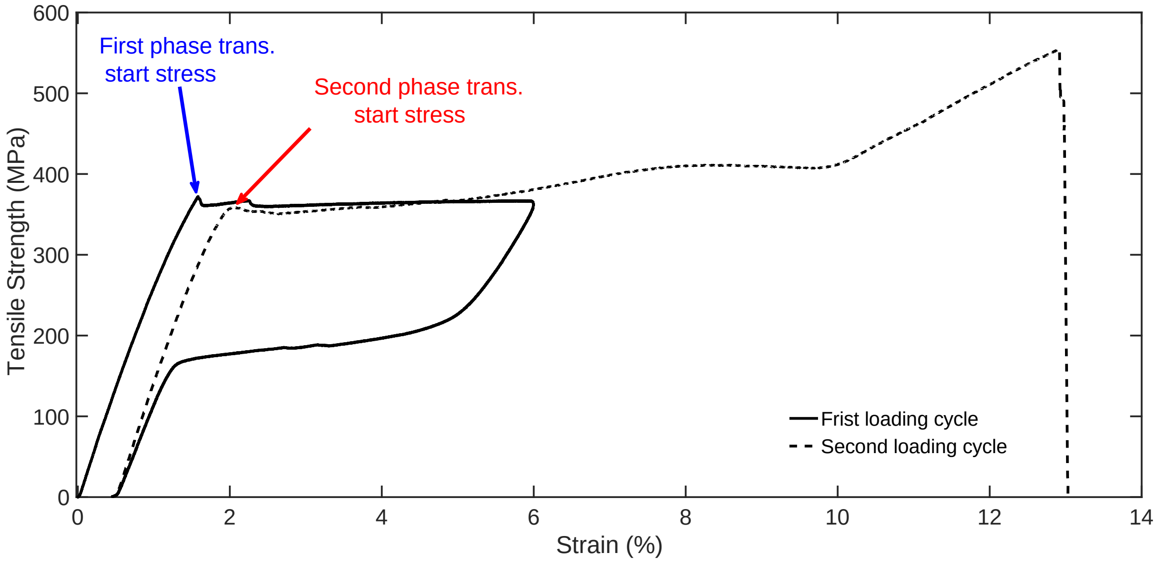


Figure 33: Stress-strain curve for the first SMA/epoxy specimen

The stress-strain behavior of one of the SMA-GNP/epoxy composites is shown in Figure 34. The phase transformation start stress levels during the first and second loading cycles were measured as 360 MPa and 339 MPa, respectively. When the specimen was further loaded up to rupture, the tensile strength of 533 MPa was achieved. The maximum strain value at fracture was measured as 12.5 %. The residual strain after first loading-unloading cycle was 0.48% for this specimen.

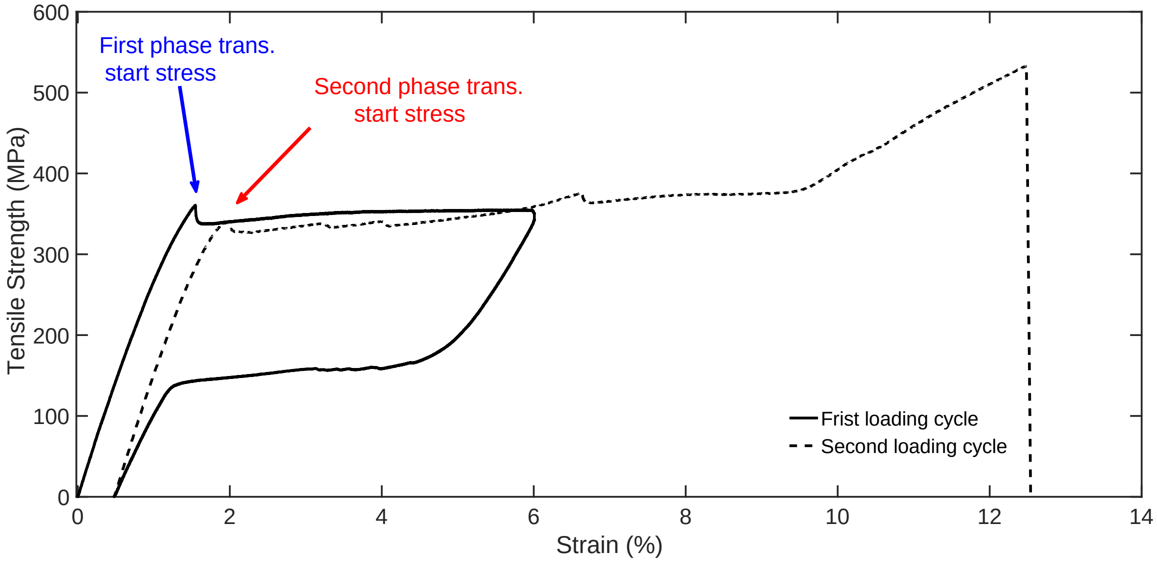


Figure 34: Stress-strain curves for the first SMA-GNP/epoxy specimen

Figure 35 shows the stress strain curves for the second specimens of SMA/epoxy and SMA-GNP/epoxy composites. For the SMA/epoxy specimens, the average phase transformation start stress level at the first cycle was 358 MPa (372 MPa for the first specimen and 344 MPa for the second specimen). The average phase transformation stress level during the second loading cycle was 344 MPa (359 MPa for the first specimen and 329 MPa for the second speciemen). The average phase transformation start stress levels for SMA-GNP/epoxy specimens for the first and second loading cycles were 362 MPa and 347 MPa, respectively.

Table 10 summarizes all the tensile results for both SMA/epoxy and SMA-GNP/epoxy composites. It can be seen that there is no significant difference in the deserved tensile behavior of both composites.

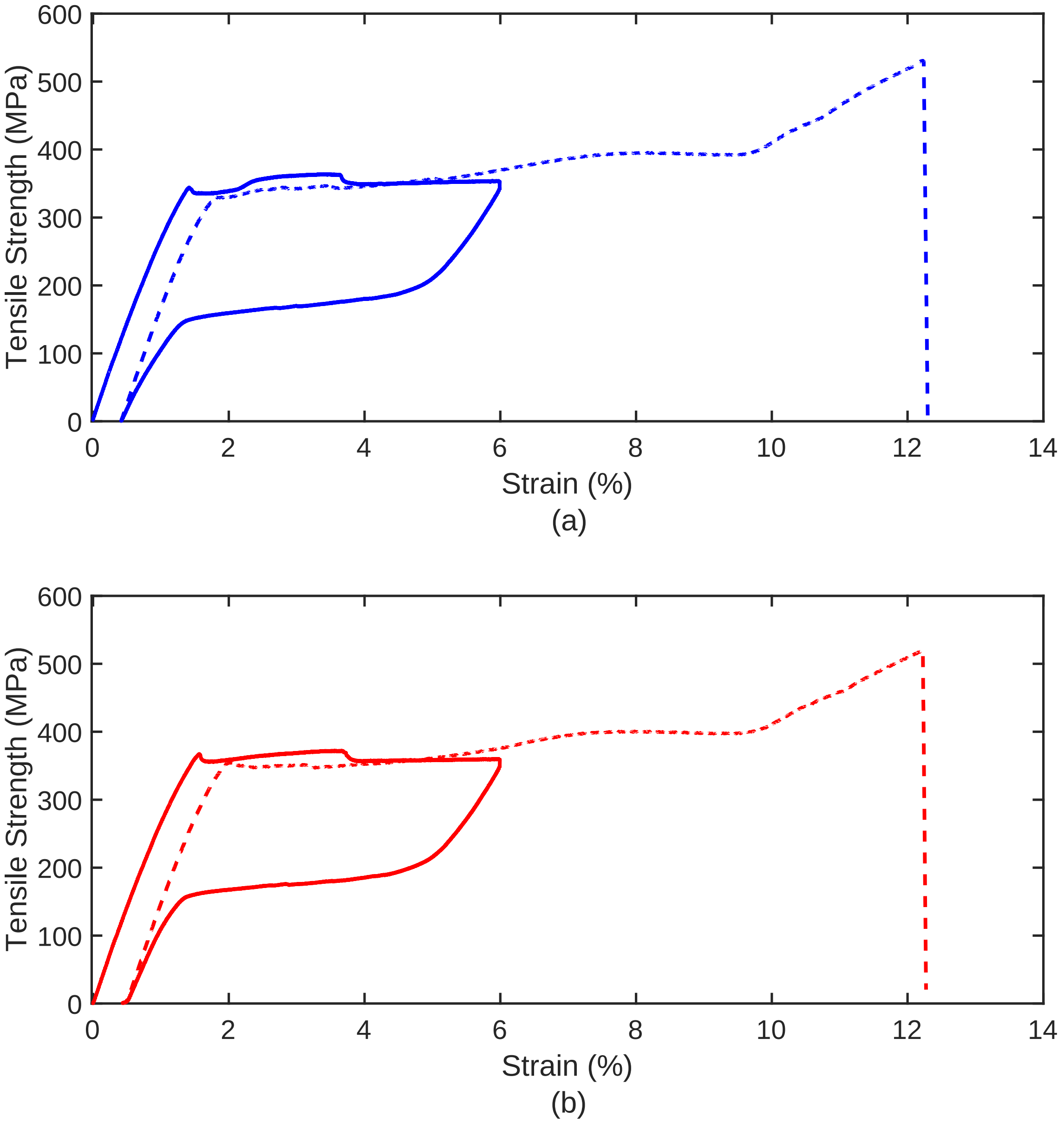


Figure 35: The stress strain diagrams for (a) the second SMA/epoxy specimen and (b) the second SMA-GNP/epoxy specimen.

Table 10: Summary of tensile behavior of SMA/epoxy and SMA-GNP/epoxy composites

	SMA/epoxy	SMA-GNP/epoxy
Phase transformation start stress level during first loading cycle	358 MPa	364 MPa
Phase transformation start stress level during second loading cycle	344 MPa	347 MPa
Tensile strength	543 MPa	526 MPa
Tensile modulus	25 GPa	25.2 GPa
Strain at fracture	12.6 %	12.4 %
Residual strain	0.43 %	0.46 %

6.4. Strain Evolution Analysis

DIC was used to monitor the strain evolution in the specimens during the testing. Figure 36 illustrates representative behavior of strain distribution of SMA/epoxy composites. It can be seen that during both first and second loading cycle a flat stress plateau was present, which indicates strain localization was occurred during the phase transformations of SMA fibers. Note that initially the strain distribution along the length of the specimen was uniform. Starting from point C, two propagating fronts moving from upper and lower end of the specimen (beginning from the grips) to the middle of the specimen was observed during loading. Note that with the unloading, the reverse transformations occurred from point H to point I and after point I the strain distributions were again uniform. During the second loading cycle, the uniform strain distributions were present up to point L where the phase transformations started and then two propagating fronts were present up to point P. After this point, the phase transformations were completed and post-phase transformation strain hardening behavior was observed during which the strain distributions were again uniform.

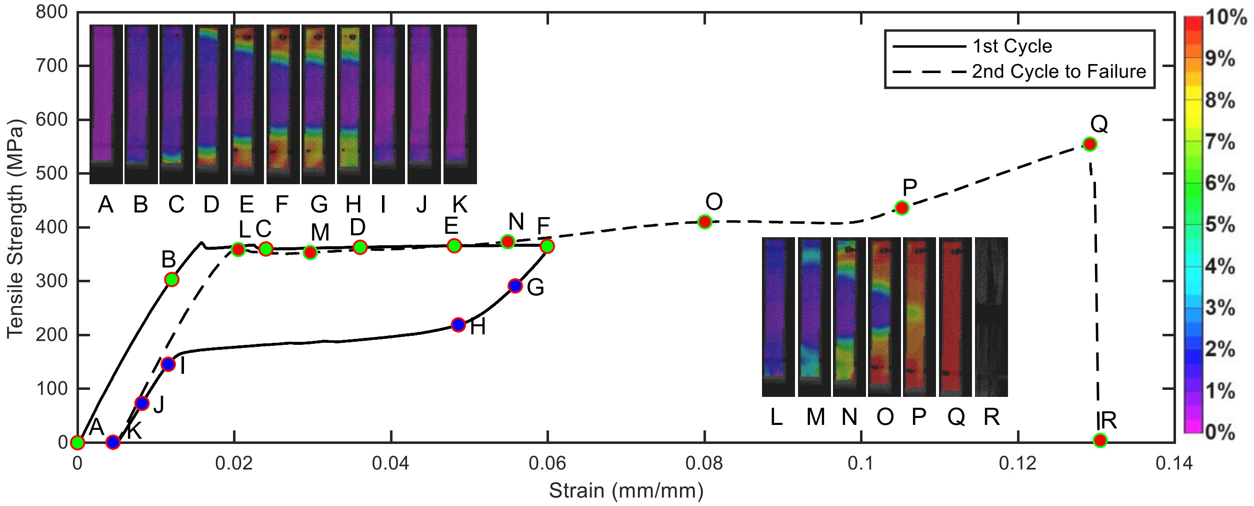


Figure 36: Strain evaluation of SMA/epoxy composites

Figure 37 shows the strain distribution for SMA-GNP/epoxy specimens. Similar to the SMA/epoxy specimens, two strain propagating fronts were initially observed at both ends of the SMA-GNP/epoxy composites. However, with loading on the stress plateau, a single front moving from top to bottom was observed. A similar strain distribution behavior was present during the second loading cycle but the propagating front were more heterogeneous during loading.

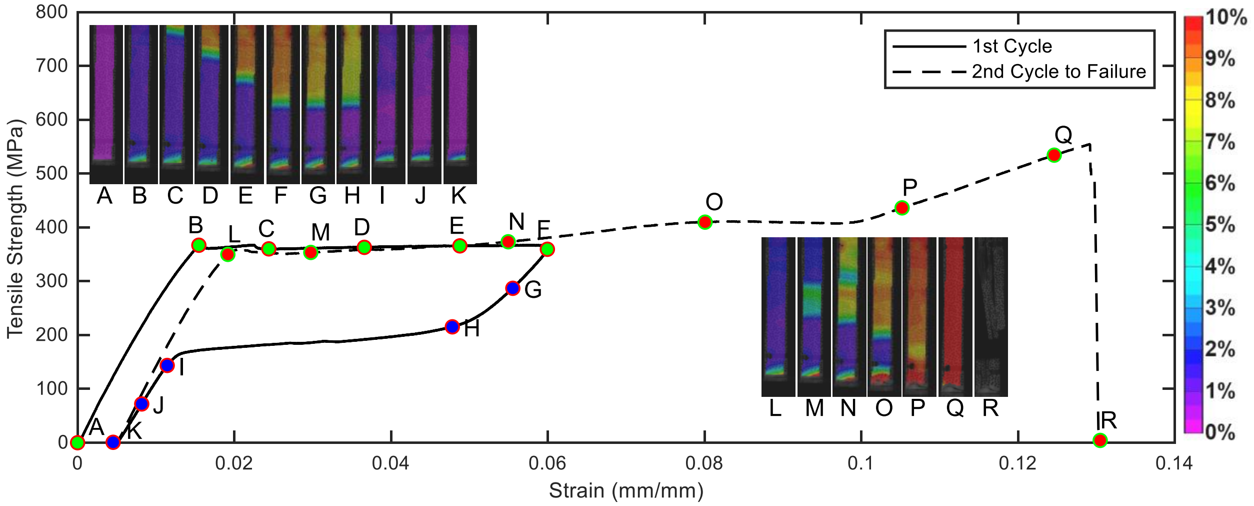


Figure 37: Strain evaluation of SMA-GNP/epoxy composites

6.5. Temperature Evolution Analysis

Thermal camera was used to monitor the temperature evolution in the specimens during the testing. Figure 38 illustrates representative behavior of temperature distribution of SMA/epoxy composites. It can be seen that during the first loading cycle, a flat temperature distribution was present, which indicates temperature localization was occurred in the phase transformation of SMA fibers. Starting from point D, two propagating fronts moving from upper and lower end of the specimen (beginning from the grips) to the middle of the specimen was observed during loading. Temperature concentration was observed until point F which corresponds to 6% strain and after point H, the reverse phase transformation was started and homogenous temperature distribution was observed at points I and J. Temperature was decreased up to 20 ^{o}C at the beginning of second loading cycle and then there observed homogenous temperature distribution again in the second phase transformation plateau. Sharp temperature evolution was observed in the strain hardening part which starts at point P. Point Q represents the temperature distribution right before rupture and it is clear from figure that the specimen was fractured at the location where the temperature has its highest value along the specimen.

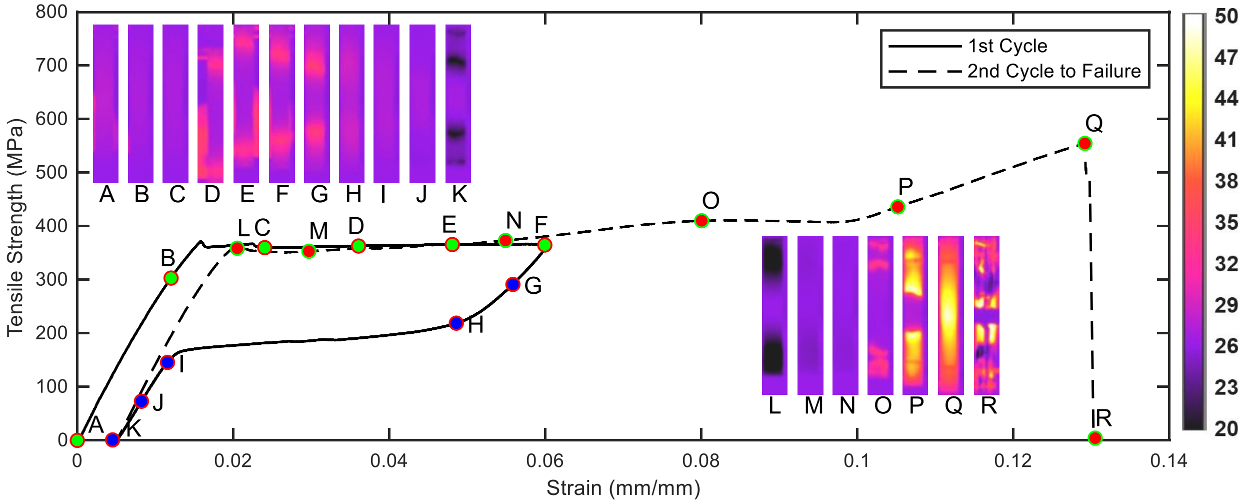


Figure 38: Temperature evaluation of SMA/epoxy composites

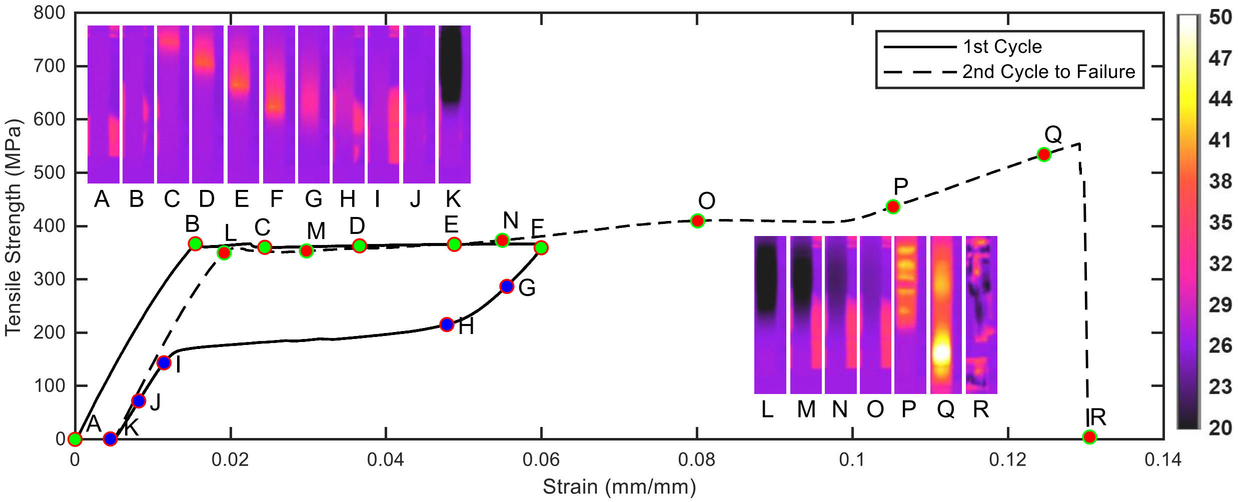


Figure 39: Temperature evaluation of SMA-GNP/epoxy composites

Figure 39 represents the temperature behavior of the SMA-GNP/epoxy specimens. Only one temperature propagating front was observed at the upper end of the SMA-GNP/epoxy composites. A similar temperature distribution behavior was present during the second loading cycle but the propagating front were more heterogeneous during loading. The temperature had its highest value at the lower mid-point of the specimen where the rupture was occurred.

6.6. Summary

In this section, superelastic shape memory alloy strands were used as fibers and neat epoxy or GNP/epoxy nanocomposites were used as matrix to develop polymer composites. The fiber volume ratio in the fabricated composites were 50%. Both SMA/epoxy and SMA-GNP/epoxy composites exhibited very good superelastic characteristics. The residual deformation in both composites after a 6% strain loading was slightly below 0.5%. The elongation at fracture was above 12%. The strain and temperature distribution were recorded and it was observed that localizations of both strain and temperature were started at the grips of the specimens and moved towards middle. The fracture was observed at the exact location where the concentration was measured to be the highest.

7. CONCLUSIONS AND RECOMMENDATIONS

This study first explored the effect of GNP addition into tensile behavior of two different epoxy resins (one brittle and one ductile epoxy). To this end, an effective method to disperse GNPs into epoxy matrix was first investigated. In particular, the use of ultrasonication alone and the combination of ultrasonication and high shear mixing for the dispersion of GNPs were studied. The effect of ultrasonication duration on the dispersion of GNPs into brittle and ductile epoxy systems were studied. GNP/epoxy specimens were fabricated by dispersing GNPs into epoxy resin through 30 min, 1 h, 1.5 h, 2 h and 3 h of ultrasonication. The dispersion of GNPs first into hardener was also studied. Various combinations of ultrasonication and high shear mixing was also considered for better dispersion of GNPs into epoxy matrix.

The results from this phase of the research indicated that the use of ultrasonication alone for above 1 hour or the use of 30 min ultrasonication followed by 60 min of high shear mixing produce largest increase in the tensile strength of GNP/epoxy composites compared to neat epoxy. It was also found mixing GNPs first into resin rather than hardener yields better results.

In the second phase of this research, the effect of GNP concentration on the tensile behavior of GNP/epoxy composites were studied. Test specimens were fabricated using both ductile epoxy and brittle epoxy with 0%, 0.25%, 0.5%, 1%, 1.5%, 2% and 2.5% of GNP concentrations by 3 different dispersion methods: (i) 2 h of ultrasonication, (ii) 1.5 h of ultrasonication and (iii) 30 min of ultrasonication and 60 min of high shear mixing. Results showed that for brittle epoxy both tensile strength and tensile modulus increase by about 15% when 0.25 wt.% GNP is added to the epoxy. However, larger increases in tensile properties were observed when the GNPs were added to ductile epoxy. For ductile epoxy, the maximum increase in tensile strength and tensile modulus was observed for the specimens with 1% GNP content. When only ultrasonication was used for either 1.5 h or 2h to disperse the GNPs, the increase in tensile strength was about 35%. However, the largest improvement in tensile strength (about 40%) was observed in the specimens fabricated by 30 min ultrasonication followed by 60 min high shear mixing. Similar to the tensile strength, tensile modulus values of ductile epoxy composites reached their maximum values for 1% GNP content. However, for the tensile modulus, the specimens prepared through ultrasonication alone produced considerably larger improvements compared to the specimens prepared by ultrasonication and high shear mixing as can be seen in Table 9.

In the last phase of this research, the selected GNP/epoxy composite was used as matrix with shape memory alloy fibers to fabricate multiscale reinforced composites. Both the neat ductile epoxy and ductile epoxy with 1% GNPs where the GNPs were dispersed by 30 min ultrasonication and 60 min of high shear mixing was reinforced with superelastic SMA fibers. All composite specimens were fabricated to have 50% fiber volume ratio. The SMA/epoxy and SMA-GNP/epoxy composites were tested to investigate tensile behavior. The loading protocol consisted of one loading and unloading cycle at 6% followed by a monotonic loading up to rupture. Results showed that both SMA/epoxy and SMA-GNP/epoxy composites exhibit very good superelastic properties with minimal residual deformations and high ultimate strain capacity. There was no considerable difference in the average tensile properties of the SMA/epoxy and SMA-GNP/epoxy composites.

Based on the finding of this study, it is recommended to further explore the mechanical characteristics of multiscale polymer composites with GNPs and SMAs. It was shown that the tensile properties of the ductile epoxy used in this study can be effectively improved through the addition of GNPs. It was also shown that SMA fiber reinforced composites that exhibit very good superelastic behavior can successfully be fabricated. However, the effect of GNP inclusion on some other mechanical properties (fracture toughness, impact resistance) and the additional functional properties (electrical resistance, sensing, thermal conductivity) of the GNP/epoxy nanocomposites and SMA-GNP/epoxy composites should also be studied. More detailed microstructural analysis is also needed to fully understand the effect of GNPs in the studied composites. The behavior of SMA-GNP/epoxy composites under cyclic tensile loading can also be studied to characterize functional fatigue behavior of these composites.

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