

PENETRATION BEHAVIOR OF COMPOSITE STRUCTURES MODIFIED
WITH SURFACE TREATED NANOPARTICLES

by

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DEDICATION

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TERMINOLOGY

Alumina nanofibers (as received)	<u>UT</u>
Alumina nanofibers (Vinyl surface treated)	<u>VT</u>
Unsaturated Polyester	<u>UPE or Resin</u>
Alumina nanofibers (as received) in UPE	<u>UT – Resin</u>
Alumina nanofibers (VT) in UPE	<u>VT – Resin</u>
Glass fiber reinforced composite	<u>Composite</u>
UT - Resin reinforced with woven glass fabric	<u>UT – Composite</u>
VT – Resin reinforced with woven glass fabric	<u>VT - Composite</u>
0.25wt% loading UT - Resin	<u>25UT - Resin</u>
0.25wt% loading VT - Composite	<u>25VT - Composite</u>

Note: First two digits divided by 100 indicate the alumina nanofiber wt% loading and two characters indicate surface treatment on alumina nanofibers.

For example, 25UT-Composite indicate 0.25% untreated alumina nanofiber filled glass composites.

ABSTRACT

Fiber reinforced composites offer a wide range of functions such as vibration damping, resistance to expansion under heat cycles, corrosion and wear resistance, fatigue resistance, impact resistance, radiation, and EMI shielding. With the continuous growth of composite structures in industry, government, civilian applications considerable interest has also grown in their ability to withstand impact resistance. Recent advances in nanomaterial synthesis functionalization has provided a possibility of tailorable properties and weight reduction of the structures without inhibiting the performance.

In this dissertation, glass fiber reinforced composites with alumina nanofiber modified polyester is developed and characterized. Effective exfoliation and dispersion of alumina nanofibers was observed using transmission electron microscopy (TEM) indicating effectiveness of optimized three roll mill parameters. The physical and mechanical properties at 0.25wt% loading level showed improvement in major properties regardless of surface treatment. Alumina nanofibers due to their fiber morphology had a greater effect on out-of-plane properties rather than in-plane properties. Viscosity an important property which has a tremendous influence on the processing difficulties of composite materials is characterized and it was noted that rise in viscosity in VT - Resin is just 58% as opposed to 158% at same loading level of UT - Resin. It is imperative from the study that use of silane coupling agents to modify the surface of alumina nanofiber had tremendous effect on mechanical properties, physical properties, and dispersion.

Wet layup was used as the manufacturing process with use of double drip pan for uniform wetting of glass fibers. The void fraction results revealed that surface treated alumina nanofiber resulted in reduced void content for a given alumina nanofiber loading. The 0.25wt% loading level of alumina nanofiber with surface treatment showed maximum improvement in composites. Fracture analysis of tested composites was performed using scanning electron microscopy and it was observed that, damage modes changed with untreated alumina nanofiber to vinyl silane treated alumina nanofiber. Adherence of matrix to the reinforcement is observed indicating enhanced interfacial interaction with surface treatment of alumina nanofibers. Thermal stability was improved with the addition of surface treated alumina nanofibers but nanofillers did not show a deleterious effect on glass transition temperature. The degree of cure calculations from differential scanning calorimetry scans revealed that silane treatment of alumina nanofibers improved the extent of crystallinity imparting stiffness contributing for enhanced properties.

Low velocity impact test results showed significant energy absorption through inelasticity or damage but not penetration. Damage in composites is observed to be progressive with possible matrix cracks leading to fiber matrix debonding and eventually delamination. The peak loads manifested were higher for vinyl silane treated alumina nanofiber modified composites. The initial stiffness values calculated for composites indicated existence of crack pinning, crack deflection mechanism contributing to maximum peak load and maximum energy absorption. The cone height formation after

impact event was found to be more than 70% of the total displacement as observed from post damage analysis of composite samples. Ballistic impact testing results according to underwriter's laboratory observed all the nine material systems qualifying for level 1 protection which has a maximum projectile velocity of 394m/s and 25UT, 75UT and 25VT material systems qualifying for level 6 protection level against maximum impact velocity of 469m/s.

1. INTRODUCTION

1.1 Impact threat

Constant threat from propelling projectiles is inevitable in army ballistic, navy ballistic and protection ballistics. An impact threat is defined as sudden application of load either during service life or during operations. For the most part, impact scenarios are distinguished between low velocity impact, intermediate velocity impact and ballistic impact. During early stages of research pertaining to understand the impact, low velocity impact is referred to as a situation where globalized deformation occurs in a material and high velocity impact is referred to as situations where deformation is localized only at the point of impact (Abrate, 1991). The categorization of impact by many authors is based on mass of impactor, incident impactor velocities and mass of impactor (Naik & Doshi, 2008; Naik, Shrirao, & Reddy, 2006). Impactor types such as tool drops, hail stones, foreign object debris, debris associated with hurricanes and tornadoes, blast debris are associated with large mass. Firearms, fragments from Improvised Explosive Devices (IED) are associated with small mass. Cantwell and Morton (Cantwell & Morton, 1991) provided a review on impact of continuous fiber reinforced composites in view of constituent properties, orientation of fabrics and stacking sequence. In the article findings, various test procedures and considering fiber, matrix, interface, fiber stacking sequence, geometrical effects are summarized. It was concluded that, strain energy of fiber, surface treatment of fibers for increased interfacial properties, reducing abrupt changes in orientation of fabric and geometry has significant effect on composite material behavior during impact event. The review also provides a base line for global deformation during low velocity impact and localized deformation under high velocity

impact. Classification based on impact damage based on three-dimensional wave propagation through the material when subjected to impact was emphasized by Olsson (Olsson, 2000). The response type is more conveniently classified by considering impactor versus plate mass ratio instead of considering impactor velocity. The response type governed by wave propagation is given in Figure 1.1. Considering impactor mass and contact times, impact response is governed by dilational wave response when subjected to high velocity impact, flexural wave and shear wave dominated response during enhanced impact times and for further-more increase in impact time results in quasi-static response behavior. It was noted that stress waves emanating from impact zone can be responsible for far field damage in composite structures.

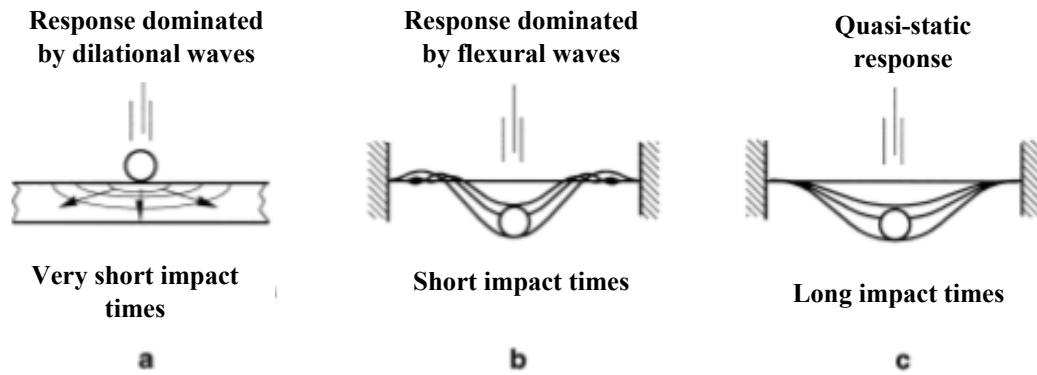


Figure 1.1: Impact responses on composite plates (Olsson, 2000)

Furthermore, classification according to velocity of impactors as represented in Table 1.1, include low velocity impacts occurring at velocities below 10m/s, intermediate velocities ranging in between 10m/s to 100m/s, ballistic velocities in the regime 100m/s to 1000m/s and hyper velocity impacts in the range of >2-5km/s (typically space debris, meteors and asteroids) (Vaidya, 2011). The velocity-based classification to justify understanding the interaction between target and projectile for efficient energy dissipation which impetuously change with velocity (Naik & Doshi, 2008; Naik et al.,

2006). Extensive reviews of impact behavior of composite and laminated structures have been provided by various researchers in past.

Table 1.1: Impact classification and damage type associated (Bartus, 2007; Cantwell & Morton, 1990; Turner, Liu, Zeng, & Brown, 2018; Vaidya, 2011)

Impact type	Velocity range	Scenarios	Damage type	Damage mitigation
Low Velocity	5m/s - 10 m/s	Tool drops.	Delaminations, Matrix cracking, Fiber breakage.	Control of fiber-matrix interface, Matrix toughening, Stacking sequence, Hybridization, Stitching, Braiding, Knitting.
Intermediate Velocity	10m/s - 50m/s	Runway and road debris, Hail impact, Hurricane, and Tornado debris.	Depending on mass deformation area varies, Specimen indentation, Matrix damage.	Use of high strain fibers, increase areal density of fabric.
High Velocity	50 m/s to 1000m/s	Broken engine parts, Turbine blades, Fragments from bombs, Shells, Mortars and Grenades, Projectile impact threats.	Fiber-matrix debonding, Tensile fiber failure of primary yarns, Elastic deformation of secondary yarns, Shear plugging, Friction between projectile and composite.	Use of high strain fibers, High strength fabrics, Woven fabric, Matrix toughening using micro and nano fillers.
Hyper Velocity	2km/s to 15km/s	Micrometeoroid strikes, Asteroid strikes on space structures, Low earth orbit strikes.	-	-

A variety of applications such as anti-ballistic clipboards, guard stations, ballistic protection for occupants of vehicles, safe rooms, tornado, and hurricane shelters require protection against propelled projectiles of varying mass and geometries. The ballistic protective materials are classified according to type of ammunition, nominal mass, and velocities which they are expected to survive. The National Institute of Justice (NIJ) standards is used explicitly for ballistic resistant materials ("Ballistic Resistant Protective

Materials - NIJ Standard 0108.01," 1985) used as armor against gun fire and not applicable for police body armor and ballistic helmets. Armor type classification, ammunition, and velocity ranges which the target is required to resist are given in Table 1.2.

Table 1.2: NIJ standards for testing and performance requirements for ballistic resistant materials ("Ballistic Resistant Protective Materials - NIJ Standard 0108.01," 1985).

Armor type	Ammunition	Nominal mass	Velocity range
I	22 LRHV	2.6 g	320 m/s
	Lead	40 gr	320 m/s
	38 Special	10.2 gr	259 m/s
	RN Lead	158 gr	259 ft/s
II – A	357 Magnum	10.2 g	381 m/s
	JSP	158 gr	852 m/s
	9mm	8.0 g	332 m/s
	FMJ	124 gr	743 m/s
II	357 Magnum	10.2 g	425 m/s
	JSP	158 gr	951 m/s
	9mm	8.0 g	358 m/s
	FMJ	124 gr	801 m/s
III-A	44 Magnum	15.55 g	426 m/s
	Lead SWC	240 gr	954 m/s
	9mm	8.0 g	426 m/s
	FMJ	124 gr	954 m/s
III	7.62 mm	9.7 g	838 m/s
	308 Winchester FMJ	150 gr	1875 m/s
IV	30-06	10.8 g	868 m/s
	AP	166 gr	1943 m/s

Abbreviations: AP – Armor Piercing, FMJ – Full Metal Jacket, JSP – Jacketed Soft Point, LRHV – Long Rifle High Velocity, RN – Round Nose, SWC – Semi-wadcutter

Underwriters Laboratory standards are exclusively used for bullet resisting materials which are used as cover materials, devices and fixtures which are required for protection against non-military armed attacks in case of robbery or hold up. Often these UL-752 standards also specify protection criteria for non-military threat such as protection for financial, commercial health care, grid security, residential, safe rooms,

schools, military recruitment centers and law enforcement (laboratory, 2005). The UL-752 standard for bullet resistant materials is provided in Table 1.3.

Table 1.3: UL-752 bullet resistant materials standard (laboratory, 2005).

Rating	Ammunition	Weight (in grains)	Velocity range (min – max m/s)
Level 1	9 mm FMJ with lead core	124	358 m/s – 394 m/s
Level 2	.357 Magnum JSP	158	381 m/s – 419 m/s
Level 3	0.44 Magnum SWGC	240	411 m/s – 452 m/s
Level 4	0.30 Caliber rifle LCSP	180	774 m/s – 851 m/s
Level 5	7.62 mm rifle	150	838 m/s – 922 m/s
Level 6	9 mm FMJ with lead core	124	426 m/s – 469 m/s
Level 7	5.56 mm rifle FMJ military ball	55	938 m/s – 1031 m/s
Level 8	7.62 mm rifle FMJ military ball	150	838 m/s- 922 m/s

Abbreviations: FMCJ – Full Metal Copper Jacket, JSP – Jacketed Soft Point, LCSP – Lead Core Soft Point, SWGC – Semi-wadcutter Gas Checked

Resistance to impact of a composite depends on various parameters such as configuration of laminate, intrinsic and extrinsic property of composite; impactor parameters such as material, geometry, velocity of impactor and angle of incidence. Conventionally, energy absorption in any material is due to elastic deformation or plastic deformation (David, Gao, & Zheng, 2009; Naik et al., 2006; Ulven, Vaidya, & Hosur, 2003). Given enough time, elastically deformed materials regain their residual strength, but plastic deformation limits load carrying capability, compromising structural integrity. Fiber reinforced polymer (FRP) composites are no longer new to the engineering community with their applications ranging from military, communication satellites, aerospace, marine to transport, sporting goods, and commodity products. Ease of manufacturing, reduced number of parts, damage tolerance and mechanical performance

stand as some key differentiators compared to legacy metal alloys along with light weighting of structural components increasing fuel efficiency. FRP composites are gaining popularity over metal matrix and ceramic matrix composites due to their high modulus, less density, low cost, and resistance to atmospheric and other forms of corrosion (Chawla, 2012). FRP composites offer a myriad of combinations with various reinforcements and matrix selection offering variety of properties such as vibration damping, resistance to expansion under heat cycles, corrosion and wear resistance, fatigue resistance, impact resistance, radiation and EMI shielding(Hosur, Vaidya, Ulven, & Jeelani, 2004; Koniuszewska & Kaczmar, 2016; Pandya, Akella, Joshi, & Naik, 2012). A laminate formed by sequential stacking of fibers and matrix consolidated to desired thickness is most common form of FRP composites for structural and high strength applications. In general, in-plane mechanical properties often characterized by static mechanical tests such as tension, compression, interlaminar shear stress, in-plane shear are adequate to design a material system. Although, out-of-plane, through-the-thickness property especially impact related property is often a difficult part of determination of behavior of the material but can be used for quality control and materials development (Mallick, 2007).

FRP composites due to their light weight, high stiffness to weight offer flexibility, agility, mobility, and lower load which are desired characteristics for military, non-military and law-enforcement applications when tackling impact threats. An impact event is a major concern regarding significant stiffness and strength reduction in composites causing a catastrophic failure of structure since composites are sensitive in direction transverse to plies or reinforcement. Impact on a composite structure results in internal

and external damages thus compromising the structure. An impact event ranges from a variety of sources such as tool drops during production, hail and debris during operation and projectile hits, bullet strikes in extreme military applications. For extensive designing of composite material system, impact characterization provides an understanding of failure modes and energy absorption when compared to other material systems under similar impact event (Chawla, 2012; Mallick, 2007).

1.2 Constituent materials

In designing a composite laminate against specific tailored applications, choice of constituent materials plays a huge role. Impact damage is a combination of delamination, matrix cracking, and fiber breakage. The choice of reinforcement in the form of fabrics provide necessary strength against fiber breakage, whereas the choice of matrix in form of polymers improve failure against delamination and matrix cracking. Impact threat is referred to loading which are suddenly applied and have a significant effect on residual properties or even worse catastrophic failure of structures. It is widely accepted that unlike traditional metal alloys energy absorption is through damage mechanisms inherited by the constituent properties.

1.2.1 Reinforcement

Reinforcement in the form of fibers are major load carrying members in fiber reinforced polymer composite structures. There are a several factors to consider in determining which type of fiber reinforcement is essential for the application (Bibo & Hogg, 1996). For example, carbon fibers which possess high stiffness-to-weight ratios are majorly considered for aerospace applications. Kevlar fibers often find application where tensile-strength-to-weight ratio is crucial. Due to anisotropic nature of fibers, they

normally possess strengths dominating in fiber direction while they are weak in out-of-plane properties like bending and torsion (Luke, 2005).

Glass fibers, Carbon fibers, Aramid fibers, Ultra High Molecular Weight Polyethylene (UHMWPE), Poly (p-phenylene-2, 6-benzobisoxazole) (PBO) fiber, Polybenzimidazole (PBI) fiber are considered some of the high-performance engineered fibers (Tam & Bhatnagar, 2006). PBO fiber and PBI fibers offer good impact resistance and are suitable for high temperature applications often hybridized with other synthetic fibers. The higher properties of above-mentioned fibers are highly dominated by monetary cost and are exclusive to high-end applications where cost is not a factor. A standard UHMWPE fiber has a tensile strength of 420 GPa, with a density of 0.97. UHMWPE fibers under trade names Dyneema and Spectra find applications in bullet-resistant vests, helmets, riot shields, integrated ballistic protection for military, marine vehicular protection because of its highly abrasive resistance, wear resistance and ballistic resistance. A major setback for UHMWPE fibers is relatively poor compressive properties which has a greater implication on residual strength after impact (Song & Lee, 2006; van der Werff & Heisserer, 2016). Carbon, Glass and Kevlar fibers are extensively used in aerospace, military, and transportation applications and since there is always impact associated in these applications these fibers are mostly studied for impact resistance. In comparison among Glass, Kevlar, and Carbon fiber for their impact resistance it was reported that carbon-based composites fail catastrophically at maximum load due to their brittle nature whereas Glass and Kevlar fibers fail in a progressive manner (Rebouillat, 2016). Glass fibers are also proven to absorb three times more elastic energy than carbon fibers. Glass fibers mainly E-Glass and S-Glass because of their low

price could make them an optimal solution for armors in which weight is not a primary concern. A comparison of selected properties and cost of high-performance engineered fibers is presented in the Table 1.4.

Table 1.4: Fiber properties and price per linear yard of ballistic fibers (Edwards, 2002; Luke, 2005; Tam & Bhatnagar, 2006)

Fiber Type	Tensile strength	Tensile modulus	Elongation	Density	Moisture regain	Cost
	Mpa	Gpa	%	g/cc	%	USD per linear yard
Glass	3500 - 4600	72 - 86	4.8 - 5.2	2.5 - 2.6	4.8 - 5.7	6.47 - 7.05
Carbon	2300 - 3400	240 - 390	0.5 - 1.4	1.7 - 1.8	0.75 - 2.4	44.95 - 59.95
Aramid	3400 - 4100	130 - 185	2 - 2.8	1.44 - 1.47	3 - 4.5	54.95
UHMWPE	$420 \times 10^3 - 485 \times 10^3$	66 - 79	3.6-4.4	0.97	<1.0	68.59
PBO	5800	180 - 280	2.5 - 3.5	1.54 - 1.56	0.6 - 2	-
PBI	400	5.6	30	1.4	15	-

1.2.2 Architecture

Architecture of the fabric used in composite fabrication has a significant role in determining end properties of composite. Different architectural types including woven, multiaxial, stitch, braids and knits have been extensively considered to impart multi-directional properties to some extent eliminating isotropic nature of laminates. Stitching process is not an integral part of the manufacturing process but an additional step where fabrics are stitched together to impart through-the-thickness reinforcement as a possibility to reduce delamination. Table 1.5 presents benefits of each type of architecture as presented by Ryan MC Dermott (McDermott, 2018) in his thesis.

Table 1.5: Fabric architecture type and characteristics (McDermott, 2018)

Architecture	Cost	Advantages	Disadvantages
Woven roving	Low	Thick for easy buildup of reinforcement sections	-
Weaving	Medium	• Best fabric stability and firmness, best resistance to in-plane shear, Higher delamination, ballistic and impact damage resistance. • Higher tensile strain-to-failure values and interlaminar toughness.	• Limited to flat laminates, Lower tension, compression, shear, and torsion properties. • Many properties are still not fully understood – durability and long-term environmental aging properties. • High strength and fatigue performance.
Braiding	High	• Higher delamination and impact damage resistance and excellent crash properties.	• Not capable of producing complex forms. • Lower stiffness and strength
Knitting	Medium	• Higher delamination and impact damage resistance. • Higher crash properties.	• Soft and hard spots in the final composite.
Stitching	Medium	• Low velocity impact and delamination resistance.	• Difficulty forming - thick preforms and curved or complex shapes.

1.2.3 Polymer matrix

Before individual fibers give away during mechanical loading, matrix plays a key role in effectively transferring stresses to adjacent fibers and keeps the fibers intact to absorb maximum energy. In a composite material, damage initiates through matrix cracking and the cracks propagate through composite material undetected. When the cracks reach fiber-matrix interface, fiber matrix de-bond occurs which eventually causes delamination. Most of the research is done on fibers and fiber architectures to increase impact resistance, because at higher strain level fibers take most of the impact load. Although matrix does not play a crucial role in impact resistance, it aids in reducing damage initiation and damage propagation to the interfaces. In this regard, most of the researchers focused on nano, micro modification of matrix and it is widely accepted in

the research community that toughened matrices contribute to higher impact energy absorption (Ávila, Neto, & Nascimento Junior, 2011; Esfahani, Esfandeh, & Sabet, 2012; Esfahani, Sabet, & Esfandeh, 2012; Kallagunta & Tate, 2019a; Pandya et al., 2012; Mohammad Hossein Pol, Liaghat, Ehsan, & Ordys, 2014; Tehrani et al., 2013).

Matrix in form of polymer are cheap, easily processable, possess excellent chemical resistance, electrical conductivity, and thermal conductivity, but also have disadvantages of low strength and modulus. A wide range of polymer matrices used in composites market are classified as thermosets and thermoplastics. Thermosets are highly crosslinked polymers which harden on curing and cannot be reprocessed. Epoxies and Phenolics are primary thermoset polymers extensively used in aerospace industry. Polyesters (PE) and Vinyl ester (VE) resins are extensively used in boat industry, transportation industry, chemical, electrical and consumer goods. Thermoplastics range from regular commodity products such as Polyethylene Terephthalate (PET), Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE), Acrylonitrile Butadiene Styrene (ABS), Polyvinyl Chloride (PVC), Polypropylene (PP) to engineered high temperature Polyetherimide (PEI), Polyphenylene Sulfide (PPS), Polyamide (PA), Polycarbonate (PC), polymethylmethacrylate (PMMA), Polyetheretherketone (PEEK) resins. The high viscosity of thermoplastic polymer melts makes it difficult to penetrate through pores of the fiber reinforcement leading to increased void content (Strong, 2006). Often this leads to use of specialized equipment such as high injection pressures and heavier molds to tackle the pressure.

Table 1.6: Properties and price of different polymer matrix (Holbery & Houston, 2006).

Polymer	Cost	Density	Elongation	Tensile strength	Elastic modulus	Izod impact
	\$/10lbs for prime resin	g/cc	%	Mpa	Gpa	J/cm
PE	17.1 - 19.5	1.3 - 1.5	2	40 - 90	2 - 4.5	0.15 - 3.2
VE	20.4 - 23.7	1.2 - 1.4	4.0 - 7.0	69 - 83	3.1 - 3.8	2.5
Epoxy	21.4 - 29.7	1.0 - 1.1	1.0 - 6.0	35 - 100	3.0 - 6.0	0.3
Phenolic	7.5 - 8.5	1.2 - 1.4	2	35 - 60	2.7 - 4.1	0.1 - 0.2
UHMWPE	12.0 - 14.6	0.92 - 0.96	100 - 400	9.6 - 39.9	0.39 - 1.37	No break - 1.3
ABS	12.5 - 13.2	1.04	25	44.81	2.34	3.73
PVC	11.3 - 12.3	1.41 - 1.52	27	51.71 - 56.53	2.83 - 2.97	0.53 - 0.85
PP	8.6 - 9.7	0.89 - 0.988	12.0 - 28.0	29.6 - 33.09	1.34	0.34 - 4.00
PEI	80.0 - 88.0	1.28 - 1.51	3.0 - 80.0	113.7 - 117.21	3.44 - 5.51	0.27 - 0.53
PA 6	13.7 - 19.8	1.13 - 1.15	35 - 300	12.4 - 94	2.5 - 3.9	16 - 654
PC	15.7 - 18.6	1.2	60	68	2.3	3.2 - 6.94
PEEK	450	1.32	10.0 - 35.0	99.9 - 110.3	3.1 - 3.80	0.53 - 0.80

1.3 Review of earlier work

1.3.1 FRP composites for impact threat

Fiber Reinforced Polymer (FRP) composites contain reinforcement made from high strength fibers and an organic matrix in the form of polymer. While reinforcement imparts load carrying capabilities, organic matrix in the form of thermoset or thermoplastic restricts the movement of fibers by binding them together and effectively distributing induced load to fibers. An important parameter which directly effects bonding and efficient load transfer between fiber and matrix is interfacial strength. The interfacial strength directly contributes to overall properties and inherent energy

absorption through different damage mechanisms (Zhou & Davies, 1995). Therefore, researchers across the world have continued to work on different reinforcement, architecture, matrix types, addition of nanoparticles and surface treatment of nanoparticles to achieve desired resistance to impact. The classification of impact has already been made earlier in this chapter. This section provides review of various fiber reinforced polymer composite systems which are researched in order to provide a good understanding of impact on FRP composites and how damage develop, how one can improve damage resistance both in perspective of different material systems and more importantly monetary value.

Composite materials absorb energy through plastic mechanisms and through interrelated mechanisms such as matrix cracking, fiber-matrix debonding, delamination and fiber breakage (Naik & Doshi, 2008; Sutherland & Guedes Soares, 1999; Vaidya, 2011). All the above-mentioned damage mechanisms have a significant degrading effect on residual strength of composite as they contribute to disruption of matrix to transfer stress efficiently to load bearing fibers (Husman, Whitney, & Halpin, 1975). Often a composite material under impact loading, suffers damage which can rarely be detected by naked eye but propagate through the material, which is termed as Barely Visible Impact Damage (BVID). Damage below BVID limit, induces significant reduction in stability and strength of composite material, leading to catastrophic failure (Dorey, 1987). Figure 1.2 provides an understanding of residual strength variation in composite materials with respect to induced damage during impact loading. Below the threshold limit, where the structure responds elastically, damage does not occur in the material. Above the threshold limit, damage starts to occur, and composite material suffers loss of strength. As the

impact velocity increases, composite material response changes from globalized structural behavior to localized behavior. This results in unchanged residual strength and loss of residual strengths is not so severe.

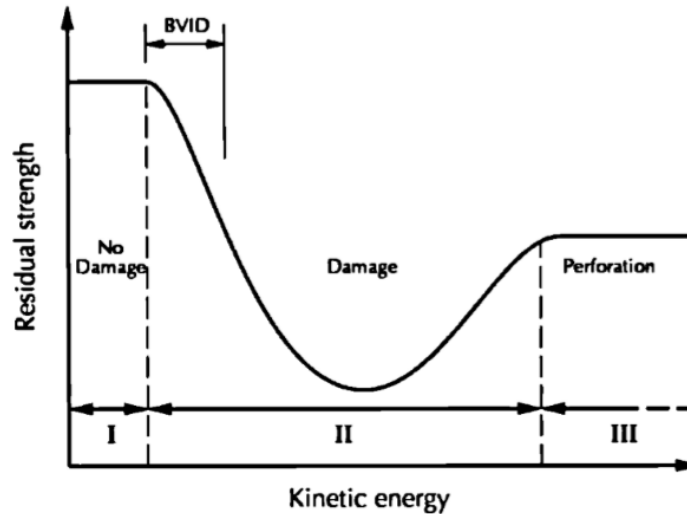


Figure 1.2: Residual strength variation and damage illustration with impactor kinetic energy (Dorey, 1987)

Naik et al. (2000), conducted extensive studies to understand the effect of plate thickness, incident impact velocities and impactor mass on damage initiation of woven fabric polymer composites. The studies included comparison of glass and carbon fiber reinforcements in the form of plain weave, balance symmetric unidirectional and balance symmetric cross ply configurations. It was noted from the studies that woven architecture resulted in high contact forces and more impact resistance. In terms of effects of thickness of laminates, it was noted that contact force and plate thickness assumed a linear relationship and in plane failure resulted in delamination mode of failure at top layer interfaces. For woven composites, it was observed that velocity had a linear effect on peak force and maximum displacement. For the purpose of analysis of velocity and mass of impactor effects on laminates subjected to impact, the parameters should be considered as independent of each other (Naik, Meduri, & Chandra Sekher, 2000; Naik,

Meduri, & Chandrasekher, 2016; Naik, Sekher, & Meduri, 2016). In an effort to understand effect of matrix ductility along with fiber architecture in form of multiaxial and woven E-Glass fabric it was noted that energy absorption is mainly dominated by fiber and effect of matrix was not significant although at lower energy levels matrix cracking is dominant failure mode. In comparison to architecture style of fiber chosen, woven composites due to presence of coarse fiber bundles acting as crack stoppers and help reduce extent of delamination (Schrauwen & Peijs, 2002). Change in fiber architecture from 2D woven fabric to using 3D woven by adding through thickness tows enhanced total energy absorption and radial spread of damage. It was observed that straightness of fibers induced by through thickness modification by tows resulted in damage extending to edge of panels. In contrast the undulation of roving's in 2D composites require more transverse deflection to straighten which is an added advantage in terms of loading the laminate to induce more delamination. Thus, although use of z-tows is significant in changing modes of energy absorption under single impact loading 2D woven composites provide excellent delamination resistance resisting the damage progress to edges of composite (Hart et al., 2017). From the studies of Zhou (Zhou & Davies, 1995) on impact damage threshold loads for E-glass/polyester, the impactor mass, target plate thickness and impact velocity bear no sensitivity to delamination. However, ply shear-out damage of E-glass/polyester laminates is significant and is a function of target geometry.

A propelling source with a low-mass-high-velocity often resulting in penetration/perforation of target is referred to as ballistic impact. Ballistic resistant protection is highly desired in military, aerospace applications. However, non-military

applications such as critical control rooms, guard stations, safe rooms, tornado, and hurricane shelters also are subjected to projectile threats. Under ballistic impact conditions, caused due to small-mass impactors, impactor loads are greater, and damage initiation is very sooner than compared to large-mass impactors at same kinetic energy levels. Small mass, high velocity impact can lead to a higher degree of local loading with a corresponding increase in damage for equivalent impact energy. During a ballistic impact threat, induced kinetic energy is absorbed through various fracture processes and plastic deformation. Structural integrity providing sufficient strength along with protection must be fulfilled by composite material.

The relatively high cost, limited repair data under field conditions and lack of extensive performance history under extreme conditions are some of key aspects needed to be explored in terms of developing a ballistic level composite armor system (Hazell, 2016). The sequence of ballistic impact energy propagation into a composite laminate is provide in the Figure 1.3. The response of material under high speed impact generates peak stresses which results in fiber breakage. As the projectile further penetrates laminate fiber is subjected to shear stresses resulting in fiber ejection and shear tensile failure of fibers. The layers in path of the projectile are subjected to further increased stresses and delaminate as stress wave spreads through the laminate. Often for this reason to enable maximum dissipation of energy into laminate and confining the projectile without perforation, the composite is designed to deform under loading to absorb incident energy.

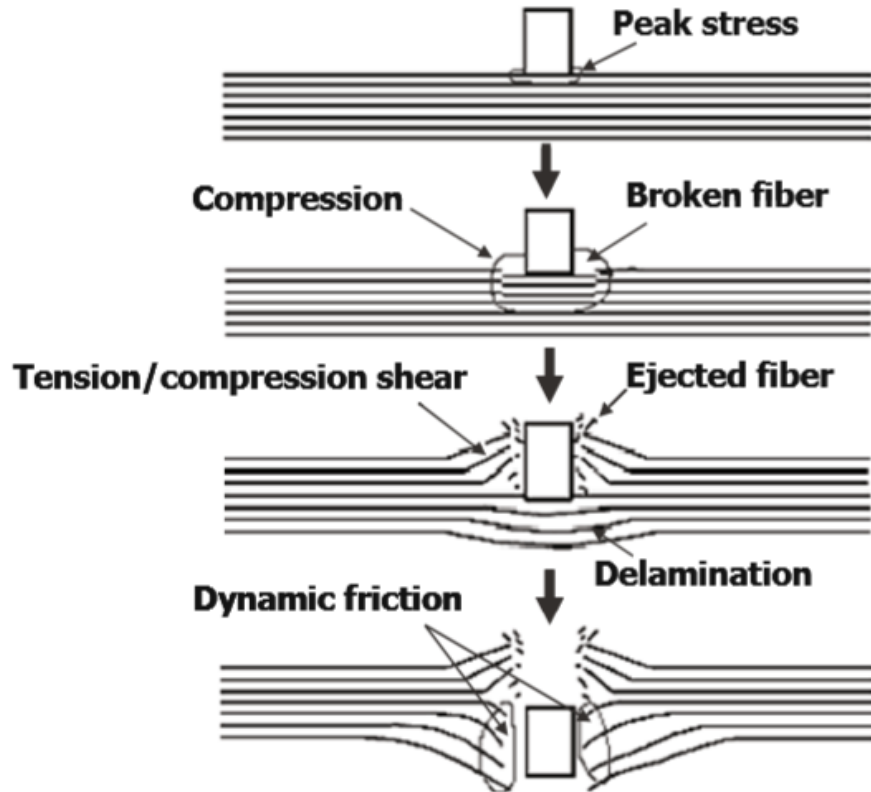


Figure 1.3: Ballistic impact on composite laminates and sequence of damage (Vaidya, 2011)

1.3.2 Modification of matrix by nanofillers

Nanomodification of polymer matrix is on high rise in research and often thermosets, thermoplastics and their blends are composed of different types of nanomaterials. Research has been published on introduction of inorganic nanomaterials into polymer matrix systems which resulted in high performance characteristics and multifunctionality beyond traditional polymer composite systems. These composites are of high interest in terms of improved thermal stability, mechanical properties, thermal and electrical conductivities, moisture resistance, charge dissipation, flame reduction and high-performance resins. However, they also induce viscosity increase which limits processability, leading to dispersion difficulties, changing from transparent to translucent and lead to sedimentation if they are not dispersed homogeneously. The homogeneous

dispersion of nanofillers in polymer is a function of fractional weight and processing techniques. The agglomerated stage of nanomaterials often can lead to inferior properties. Methods such as ultrasonication, mechanical mixing, high shear mixing, solvent blending are some of the processing techniques aim at uniform dispersion of different nanomaterials into thermoset matrixes. Hot melt compounding techniques such as single screw extrusion, twin screw extrusion for example are aimed at dispersion of nanomaterials into thermoplastic matrix systems. Depending on the as received stage of nanomaterials require processing techniques or a combination of processing techniques for property enhancement. For example, nano clay in form of platelets and carbon nanotubes require high amount of shear forces to exfoliate and de-bundle aggregates for efficient enhancement in resulting nanocomposites.

While using nanoparticles, apart from the interface of matrix and fiber, the interface of nanoparticles with matrix phase also play a decisive role on their dispersion and adhesion. The interface of nanofillers and matrix is controlled by dispersion state of nanofillers in the resin (Dasari, Yu, & Mai, 2016; Koo, 2006). Figure 1.4 gives an illustration of nanofiller classification based on their morphology and existence of nanofillers in matrix medium. The unmixed and intercalated nanofiller state gives rise to stress concentration points, which have a negative effect on mechanical properties of resultant nanocomposites. In truly exfoliated state where nanofillers are completely bind by matrix, efficient stress transfer between two constituents takes place resulting in desired enhanced mechanical properties. This is true for any morphology of nanofiller to play a positive role in matrix toughening.

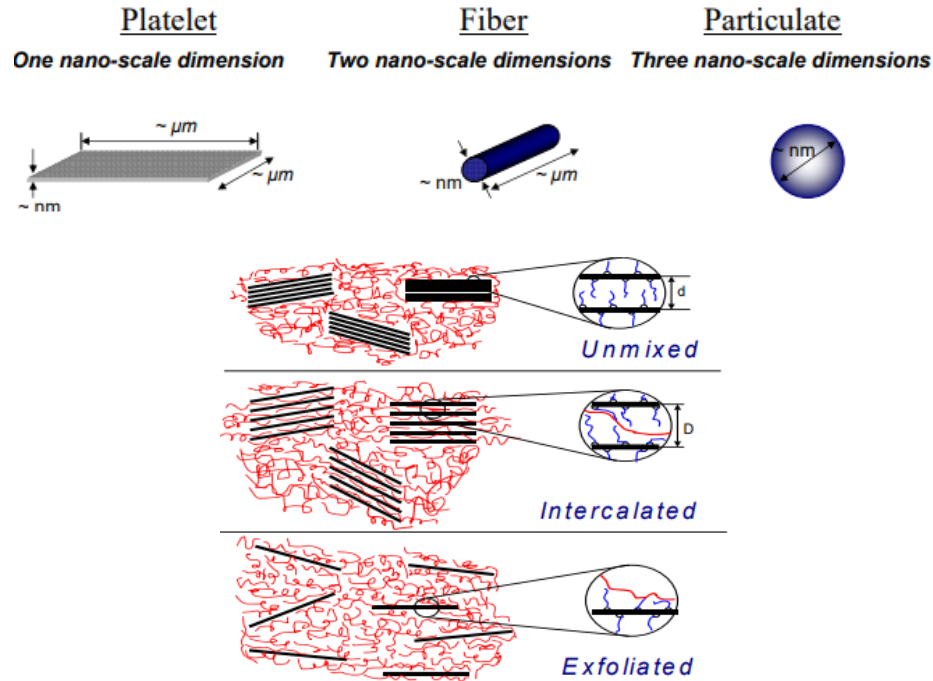


Figure 1.4: Illustration of types of nanofillers based on their morphology and dispersion state of nanofillers in the matrix (Koo, 2006).

Nanoclay, nano alumina, nanosilica stand among the widely used nanoparticles to increase stiffness and toughness in polymer systems offering monetary value against high cost carbonaceous nanomaterials such as carbon nanotubes, nanographene and carbon nanofibers. Carbonaceous nanomaterials due to their strong interactions cause agglomeration at higher loading levels, often requiring time consuming and high energy dispersion routes for beneficial property enhancement. Addition of 1% to 8% concentration of nanosilica to the two-part epoxy system has showed significant improvements in mechanical and thermal properties of resultant nanocomposites (Kinloch et al., 2003). Later studies revealed that up to 10wt% concentration levels can be used without agglomeration difficulties and chemical reaction between silanol groups of nanosilica - epoxy groups can enhance interlaminar shear strength. Increase in critical crack length and increase in fracture toughness is evident with 10wt% nanosilica

addition. Further studies on understanding effects of hybridization of nano and micro fillers on mechanical and thermal stability properties revealed the synergistic effect between the fillers used (Kinloch et al., 2005). Nano alumina in form of spherical particles are widely used in enhancing mechanical properties of fiber reinforced composites. Effects of 1wt% to 5wt% loading level of nano alumina particle modification of epoxy and reinforced with glass fiber are studied and a linearity of tensile strength to nanofiller loading was observed.

Alumina nanofibers in their as received form are studied for their effectiveness in energy absorption under low velocity impact loading, at impact energies of 29J, 39J and 50J by Kallagunta and Tate (Kallagunta & Tate, 2019b). The study provides a comparison between effectiveness of alumina nanofibers at 2.5wt% and nanosilica particles at a loading level of 10wt%. It was noted that alumina nanofiber at 2.5wt% loading level manifested slightly higher peak loads and normalized energy as compared to 10wt% nanosilica composites, at higher energy levels. With the aid of thermography and microscopy images damage was studied in resulting composites and it was observed that alumina nanofiber modified composites showed damage dissipation without causing extensive delamination indicating their effectiveness energy dissipation. As a result, the stiffness values were maintained indicating enhanced residual strengths at lower loading levels making it a more feasible nanofiller. However, it was noted that this behavior can be enhanced at furthermore low loading levels if efficient dispersion and stress transfer can be facilitated between nanofiller and matrix (Kallagunta & Tate, 2019b). A prominent method being considered for efficient dispersion of nanoparticles in the matrix by use of coupling agents, surfactants to provide surface groups which can efficiently

bond to the continuous matrix phase. Silane coupling agents are most extensively used for providing a reactive surface on nanomaterial for efficient bonding with host polymer. Depending on target matrix, a wide variety of organo-functionalities are at disposal.

1.4 Material system

1.4.1 E-Glass

Glass fibers are used in majority of industrial, wind blades, composite pipes, marine, aerospace, sporting goods, abrasion resistant, radiation and electromagnetic shielding applications. Glass fibers are regarded as cost effective solutions offering good mechanical performance and can be used with a wide selection of polymer matrix systems. Unlike carbon fabric reinforced composites which are brittle, expensive, and low impact resistance, glass fiber reinforced composites offer more ductility, high impact resistance and an economic solution. Glass fibers are not compatible with more resins due to their hydrophilic nature. Hence, glass fibers are sized using silane agents where in silicon on one end bonds well to fiber and organic ends bond with resin aiding good adhesion. Sizing is applied to glass fibers during the process in composition of 5-15% depending on end application (Thomason, 2019). Glass fibers possess about 5.0% strain-to-failure, when compared to other high-performance fibers, making it highly suitable for use in structures to absorb impact or abrasive forces. E-Glass fibers offer tensile strength much stronger than steel and in par with industrial grade fibers at moderate cost. The global market for glass fibers used in composites is approximately 5million MT per annum, while estimates on high end for carbon fiber is less than 2% of size of glass fiber market size (Brosius, 2016a). The composition and properties for E-glass which are of main interest is listed in Table 1.7. E-glass fabric with 0/90 biaxial plain weave

architecture from Owens Corning which have an aerial weight of 888 g/m² is used in present research.

Table 1.7: Properties of E-glass fibers

Density	Youngs Modulus	Tensile Strength	Ultimate Tensile Strain	Wave Velocity in Fiber	
				Longitudinal	Transverse
g/cc	GPa	Gpa	%	m/s	m/s
2.5-2.8	75-90	2.4-4.2	4.5-5.0	480-631	5400-6000

1.4.2 Unsaturated polyester - UPE

Thermoset resins are extensively used in high performance applications due to the excellent in-plane and out-of-plane mechanical properties. Thermoset resins offer excellent adhesion, high thermal stability, high chemical resistance and complete wet out of fabrics. Thermosets often require addition of curing agents to fasten the curing process. Unsaturated Polyester (UPE) resin has been commercially available since 1941 and are extensively used along with glass fibers in radar domes, ship building industry. Isophthalic UPE resin is commonly used in structural composites. Free radical initiation is primary polymerization reaction process which promotes curing of polyester resin. In general, hydroperoxides (Methylethylketone Peroxide) along with metal salts (Cobalt naphthenate) are used as initiator and promoter, respectively. The major disadvantage of using metal salt promoters is the exothermic reaction which has an effect of heat of reaction. The lower thermal conductivity of polymers does not allow excessive heat to transport out of the material during polymerization causing thermal residual stresses and formation of gas bubbles (Fink, 2013). To eliminate this, in the present research Benzoyl Peroxide (BPO) is used which promotes curing through free radical polymerization using

heat as an external aid. Following the manufacturer's instructions, the curing temperature of 80°C (180°F) was used.

1.4.3 Alumina nanofibers - ANF

The patented synthesis route developed by ANF Technology Ltd, produce alumina nanofibers in the form of highly ordered arrays of co-aligned fibers with a spacing of 20 to 40nm between each fiber under the trade name NafenTM. Nanofibers of pure Alumina in gamma phase with surface area >150m²/g, average fiber diameter of 7nm -10 nm, aspect ratio of 30:1 to 100:1 and thermal stability of up to 1100°C have proven to enhance properties of polymers, ceramics, composite materials , concrete and extending to fine abrasion materials, dielectric materials, light weight and 3D printable materials. Alumina nanofibers under the trade name NAFEN are unique ceramic nanofiber materials with their potential applications in automotive industry claiming fire resistance, high temperature stability, abrasion resistant, corrosion resistance, impact and fracture resistance properties imparted when used as nanofillers in polymers. The versatility of these nanofibers has enabled their use in high performance adhesives, sealants incorporated to toughen thermoset and thermoplastic polymers for applications in commercial and military aircraft imparting dielectric, thermal conductivity and sensor shielding properties along with enhanced mechanical properties. NafenTM nanofibers are possible to be functionalized with various silane, titanate, phosphonates, inorganic substances according to the need in further enhancing properties. Internal research and development studies showed promising results in enhanced tensile, compressive, compressive after impact and ballistic properties of composite material systems with loading concentrations ranging from 0.36% to 2.5wt%.

Raikitin and Grodensky were the first authors to report studies on effects of alumina nanofibers on mechanical properties of epoxy, polyamide, polycyanurate, polyester and Polyvinyl butyral. Investigations on flexural property of nanocomposites modified with alumina nanofibers into polycyanurate reported an increase in maximum load carrying capability by 70% and modulus increase by 40% at 5wt% concentration. The linearity in property enhancement with increase in loading concentration is observed (Aleksandr Rakitin, 2014). In case of nanomodification of epoxy resin, a loading concentration of 0.1wt%, work of fracture and flexural strength were enhanced by approximately 266% and 136% respectively. In case of UV-curable polyester acrylate coatings as compared to nano silica at 5wt% concentration alumina nanofibers proved to be more effective. While it was noted that nanomodification enhanced properties of polymer systems, a comparison between 5wt% loading level of alumina nanofibers and 5wt% nanosilica on tensile properties such as Youngs modulus, tensile strength and elongation at break showed an improvement by 17%, 46% and 86% respectively. When used in thermoplastic polymer such as nylon addition of 0.5wt% alumina nanofibers increased the yield limit by a factor of 2.

Due to the uniqueness of fiber morphology of this type of nanoparticles, there is limited literature available on effects of alumina nanofiber modified nanocomposites. Hence, it provides a promising area for study of this new type of nanoparticles on static mechanical, low velocity impact and ballistic impact properties.

1.5 Objectives

Based on the above discussions in terms of affordability, compatibility and application which require high performance against ballistic impact resistance, E-glass reinforced polyester composites seem to be a viable option. The advantage of

nanotechnology can be used to replace traditional material system by modifying the existing system with nanofillers for enhanced performance. Alumina nanofibers because of their unique fiber like morphology and being a ceramic based nanofiller are selected for this research. Since there is almost no documented literature on composites modified with this class of nanofiller, the findings in this research would be of significant contribution to technical community. Effective utilization of nanofillers in the polyester resin system remain unexplored for enhancement in impact resistance of non-military applications such as storm shelters, safe rooms. This research aims at exploring use of alumina nanofibers to enhance the properties of glass fiber reinforced polyester composite laminates. The overall goal of research is to develop composite laminates which will improve level of protection offering the possibility of same protection at an overall reduced mass, or an improved level of protection at the same mass as specified by Underwriters Laboratory Level-I and Level-6 standards.

The specific objectives of the present research are:

1. Effective dispersion of alumina nanofibers in unsaturated polyester resin using three roll mill (calendaring) approach.
2. Study effects of alumina nanofibers and surface treatment of alumina nanofibers on physical, mechanical properties of unsaturated polyester resin.
3. Manufacture good quality composites with 0/90 woven E-Glass fabric as reinforcement and nanomodified unsaturated polyester using a combination wet layup and compression molding press.
4. Study the effects of nanomodified polyester resin on static mechanical properties of glass reinforced polyester composites.

5. Study the effects of nanomodified polyester resin on low velocity impact response of glass reinforced polyester composites.
6. Study the effectiveness of developed nanomodified polyester glass composite material system against ballistic threats of UL level 1 and level 6

This dissertation includes six chapters. The first chapter provides an overview and background information on available material constituents, literature by various sources and research gaps which has long evaded the ballistic impact industry. The alumina nanofiber dispersion into polyester resin was fine-tuned and bulk physical properties of nanocomposites are studied to determine the effects of alumina nanofibers in the base resin. Chapter 2 presents optimized dispersion parameters, balance between physical and mechanical parameters as a function of loading content and surface treatment. Chapter 3 discusses manufacturing process using a combination of wet layup, compression press and efficiency of the process in terms of voids generated in cured composite. The static mechanical property disparity with variation in loading content is discussed in chapter 3. Chapter 4 discusses thermal stability characterization of the formulations using thermogravimetric analysis at multiple heating rates and differential scanning calorimetry analysis. Additionally, activation energies were determined using two isoconversion methods to further study thermal stability of the nanocomposites. Chapter 5 discusses the findings of glass reinforced polyester composites against low velocity impact loading and the damage in terms of delamination threshold loads. Chapter 6 reports findings related to ballistic impact on the nanomodified glass polyester composites according to underwriters' level 1 and level 6 testing specifically against 9mm FMJ projectile. Figure 1.5 summarizes chosen experimental studies in dissertation.

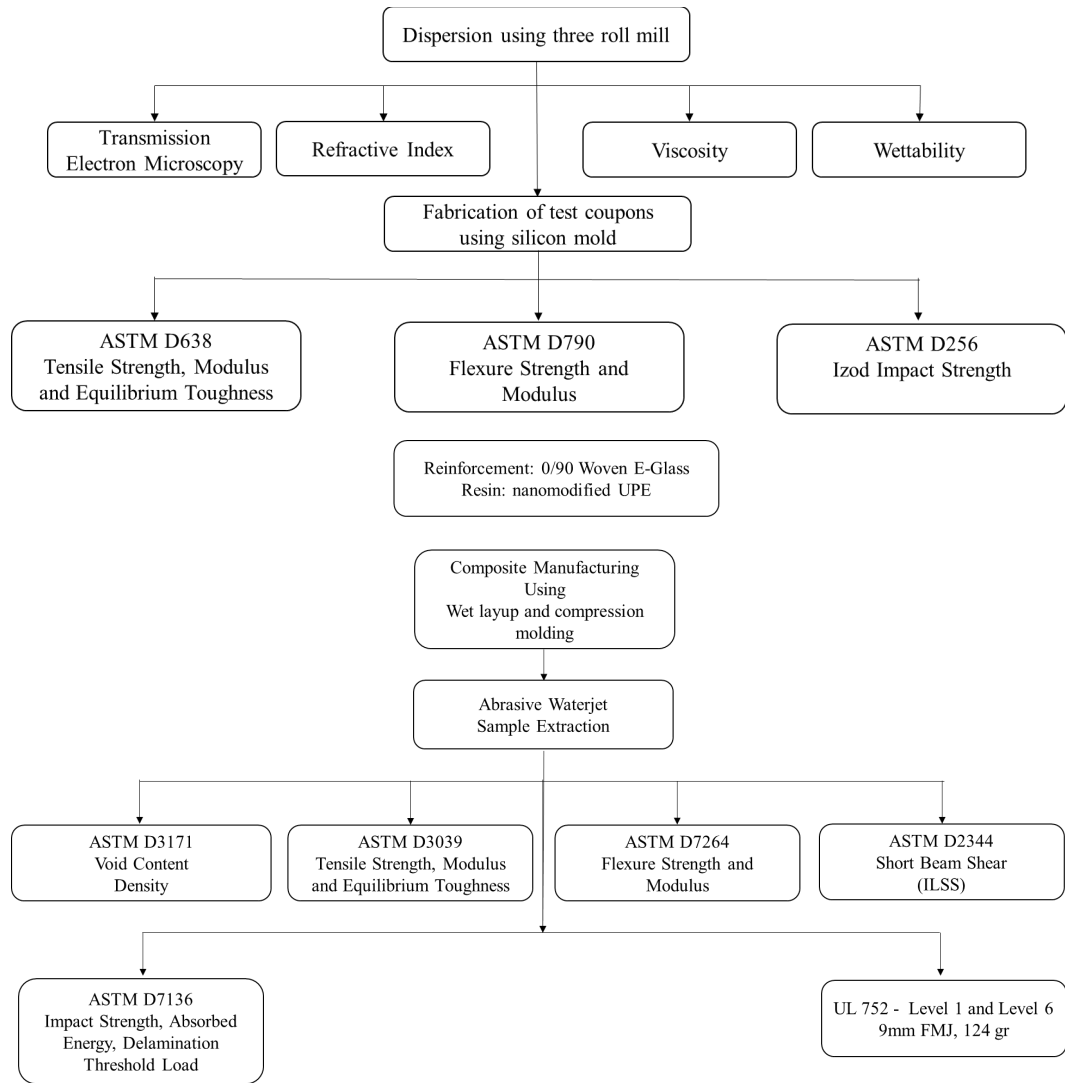


Figure 1.5: Experimental procedure illustration

2. ALUMINA NANOFIBER (ANF) FILLED POLYESTER NANOCOMPOSITES: PROCESSING, FABRICATION AND PERFORMANCE EVALUATION

Nanoparticle addition to polymer systems is a viable approach implemented to enhance mechanical performance for engineering applications. Nanoparticle owing to their high specific areas promote efficient stress transfer and thus have a positive effect on toughness and stiffness of the resulting nanocomposite. However, incorporation of nanoparticles into polymer matrix gives rise to unwanted complications such as increase in viscosity, agglomeration and poor exfoliation thus giving rise to negative effects on resultant material system. Unsaturated polyester resin exhibit moderate properties, ease of processing and are of economic value, which makes them highly suitable for many industrial applications. Unsaturated Polyester resin SIL47DA-2949 manufactured by Interplastic Corporation with a viscosity of 396cPs is used for research. The isophthalic unsaturated polyester resin is composed of 50% w/w Styrene and 50%w/w Vinyl Toluene as reactive diluent. Benzoyl Peroxide obtained from Sigma Aldrich is used as curing agent which promoted free radical polymerization using heat as external stimulator.

Nanoparticle modification of unsaturated polyester is less explored field and very few publications showing promising results are not sufficient to completely evaluate the effect of nanofillers on mechanical properties of the resin. Hence present research aims at understanding the effects of alumina nanofibers on physical, morphological, and mechanical properties when incorporated into unsaturated polyester resin. In addition to use of alumina nanofibers without any surface modification, vinyl silane treated alumina nanofibers are studied for their effectiveness on above properties. The silane agent used for study comprised of Vinyl Trimethoxy Silane (VT). For this study, concentration

levels of 0, 0.25wt%, 0.5wt%, 0.75wt% and 1wt% are chosen for both categories. Since there was no earlier work published, loading levels were selected based on the suggestion from the chemist of ANF Technology and keeping in view the increase in processability issues at higher concentrations.

2.1 Processing

2.1.1 Calendaring approach

Three roll mill calendaring approach as shown in Figure 2.1 is used as the main dispersion technique throughout this study. Dispersion of the alumina nanofibers at required concentration levels into unsaturated polyester resin was done by three roll mill apparatus manufactured by EXAKT technologies. The three adjacent cylindrical rolls each turning at different velocities, result in pure shear providing efficient means to de-bundle nanoparticle agglomerates. The feed and apron rollers rotate in same direction, whereas the roller in center rotate in opposite direction. The material is fed between feed and center roller, and material then flows through the adjacent rollers and is collected by using a scraper tool in contact with the apron roll. The mill is equipped with electronic speed control and provision to set the gap between rollers during operation. The gap between feed and apron roller is set at 25 μ m, 15 μ m and 7.5 μ m respectively for three passes.

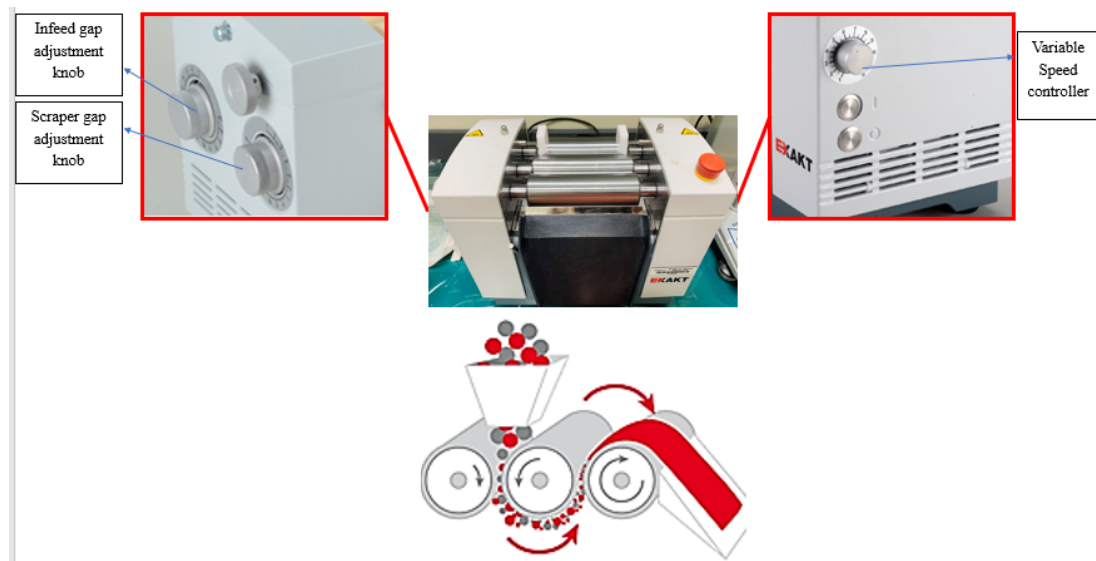


Figure 2.1: Three roll mill and illustration of dispersion using calendaring approach
(Courtesy: www.exaktusa.com)

2.1.2 Sample fabrication

The untreated alumina nanofiber modified polyester resin (UT – Resin) and vinyl silane treated alumina nanofiber modified polyester resin (VT – Resin) were cast into silicon molds as per ASTM standards and were cured in oven at 80⁰C as per specifications of chemist at Interplastic Corporation. The cured modified polyester coupons were post cured for three hours at 110⁰C in programmable oven. The silicon molds are made from silicon molding compound which can withstand high exothermic temperatures occurring during curing and post curing. Silicon molds are advantageous over metal molds since there is no thermal induced stresses into samples. Figure 2.2, Figure 2.3 and Figure 2.4 represent molds prepared according to ASTM D638 ("Standard Test Method for Tensile Properties of Plastics,") for tensile testing, ASTM D790 ("Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials,") for flexure testing and ASTM D256 ("Standard Test

Methods for Determining the Izod Pendulum Impact Resistance of Plastics,") for izod impact testing.

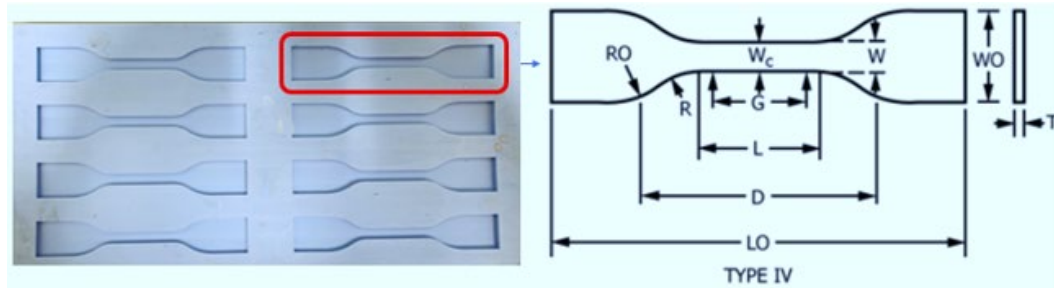


Figure 2.2: Tensile test coupons: Silicon mold for casting samples according to ASTM D638 standard ("Standard Test Method for Tensile Properties of Plastics,")

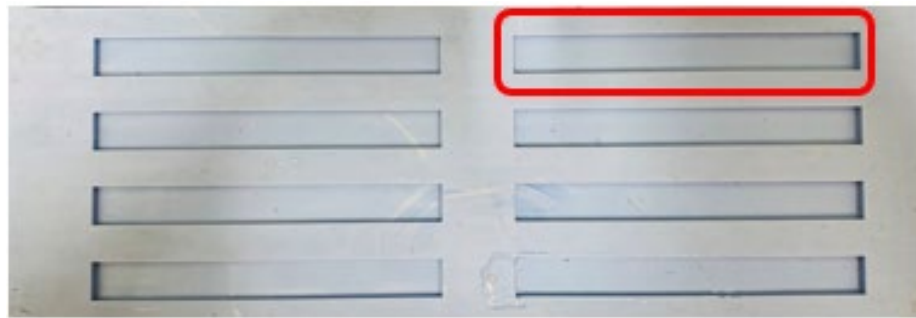


Figure 2.3: Flexure test coupons: Silicon mold for casting samples according to ASTM D790 standard ("Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials,")

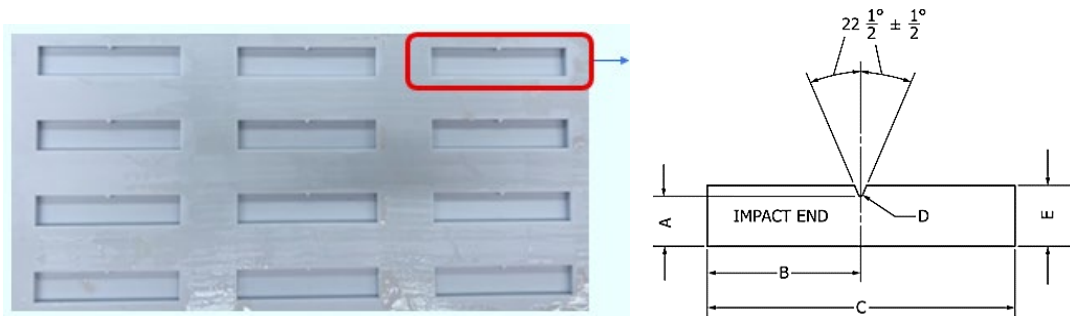


Figure 2.4: Izod test coupons: Silicon mold for casting samples according to ASTM D256 standard ("Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics,")

2.2 Characterization

2.2.1 Transmission electron microscopy

The dispersion state of alumina nanofibers in polyester is characterized by TEM. Thin sections of polyester modified with alumina nanofiber were obtained by using Leica Reichert Ultramicrotome with a glass knife at room temperature. The sections were then placed on 400 mesh copper grids. The grids were then transferred into JEOL JEM 1200EXII TEM for high resolution imaging.

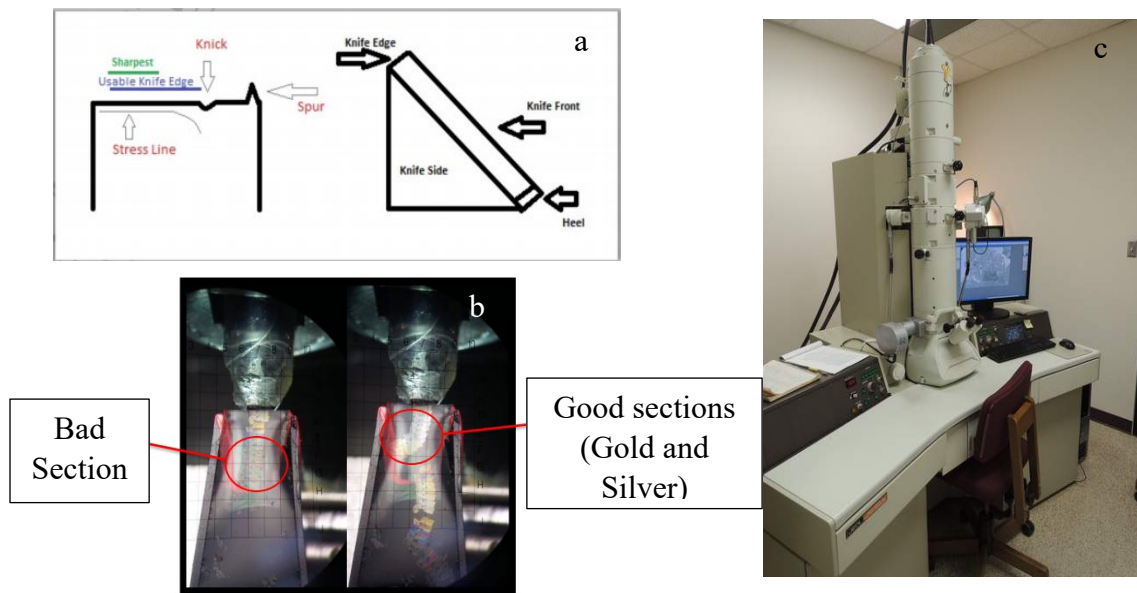


Figure 2.5: Grid preparation using (a) glass knife and (b) ultramicrotome to view in (c) TEM

The preparation of samples for viewing in TEM is illustrated in Figure 2.5 along with equipment. The illustration shows the glass knife geometry used for sectioning samples and differentiation between good samples and bad samples (Figure 2.5 b). Good sections are often samples having thickness up to 70nm, which provide enough transmission of electrons for better viewing results.

2.2.2 Refractive index

The refractive index measurements were conducted using Bausch and Lomb Abbe-3L refractometer (Figure 2.6). The uncured sample after dispersion at required loading levels of alumina nanofiber is carefully placed on the prism to form a thin layer and the prism was closed. The lamp was adjusted so that the prism illuminates, and refractive index is recorded.

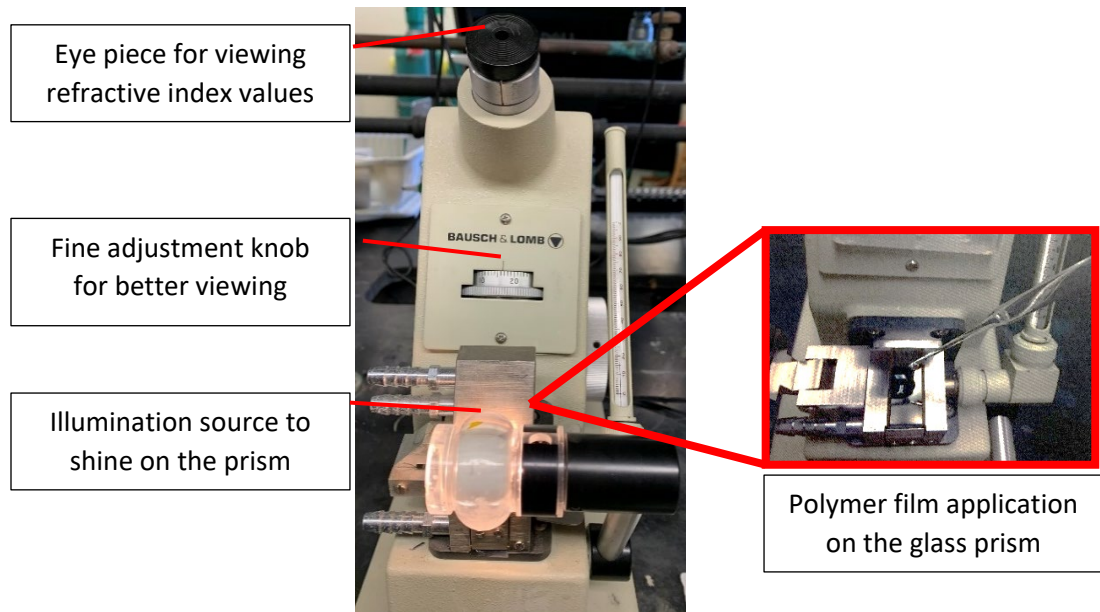


Figure 2.6: Bausch and Lomb Abbe 3L Refractometer

2.2.3 Viscosity

The effects of adding alumina nanofibers and presence of surface treatment on viscosity of unsaturated polyester resin were studied using Thermo Scientific Haake Viscotester. Along with the effects of surface treatment, variation in viscosity with concentration of alumina nanofibers is studied and reported. 15mL of the sample was placed inside immersion tube and a rotor (coaxial cylinder) was used to measure the shear rate and viscosity. All the samples are tested at room temperature. The shear rate vs shear

stress plots were graphed, and viscosity is measured as the slope of curve. The illustration of equipment and components are shown in Figure 2.7.

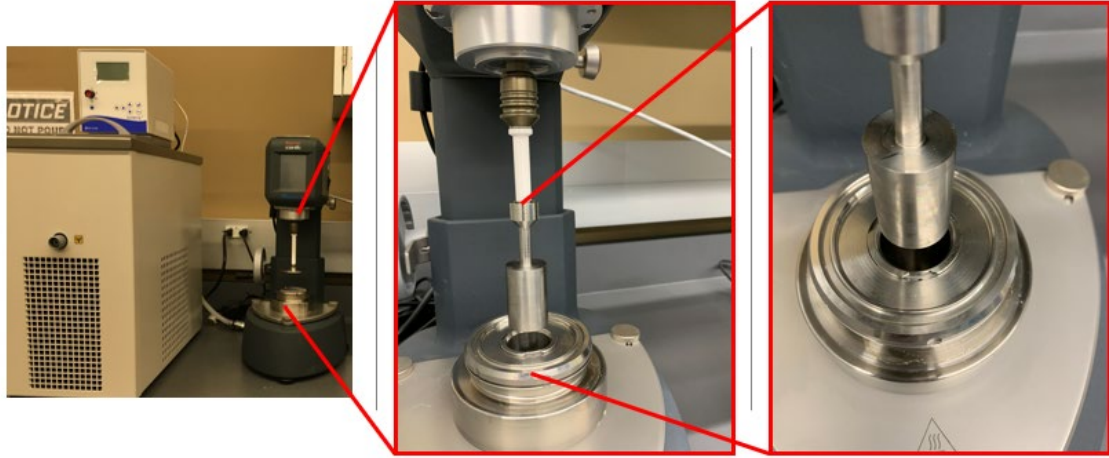


Figure 2.7: Haake Viscotester for viscosity studies

2.2.4 Wettability

Raame-Hart Contact Angle Goniometer as shown in Figure 2.8 is used to measure contact angle to understand wettability changes due to incorporation of alumina nanofibers. The alumina nanofiber modified polyester resin droplets are carefully dropped on the glass polymer composite substrate and with the aid of a telescopic eyepiece angle between resin and substrate is measured.

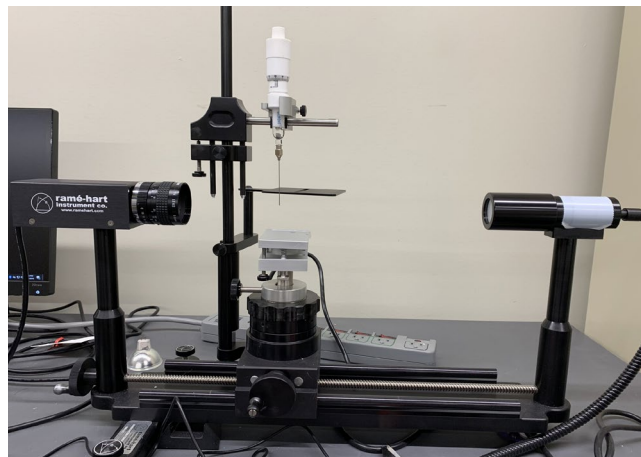


Figure 2.8: Raame-Hart contact angle goniometer.

2.2.5 Mechanical testing

2.2.5.1 Tensile test

The tensile property of alumina nanofiber reinforced unsaturated polyester were carried out in accordance with ASTM D638 ("Standard Test Method for Tensile Properties of Plastics,") using an united testing systems electro mechanical test system. Samples were cast into type IV specimens with overall length of 115mm and overall width of 19mm. The cross head speed of 1mm/min was used. Average values and error bars were calculated based on 5 tests for each formulation.

2.2.5.2 Flexure test

The flexure property was in accordance with ASTM D790 ("Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials,") and was carried out on united testing systems electromechanical test system. The cross head speed was chosen as 0.10mm/min according to the standard. At least five samples were tested for each formulation and average values are tabulated.

2.2.5.3 Izod impact test

Izod strength of nanocomposite for all the formulations was tested using Instron CEAST 9340 drop weight test bench in accordance with ASTM D256 ("Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics,"). The dimension of test coupon was 100mm x 10mm x t and a 2.5mm deep notch was cut on each specimen. Five specimens were tested for each formulation. All samples were conditioned at room temperature and 50% RH for atleast 48hours before testing.

2.2.5.4 Statistical analysis

For statistical analysis it is important to select number of factors and levels which will have a significant effect on the response. In the process under consideration, the

properties are identified as response and loading content, surface treatment are factors.

Table 2.1 provides details on the factors considered and their levels.

Table 2.1: Factors considered along with their levels

Factor	ANF	Surface treatment
Area	Material	Material
Type	Variable	Variable
Levels	0 25 50 75 100	0 1

The study is aimed at finding the significance of property response as an effect of loading and surface treatment as factors. Process parameters are not considered for the purpose simplifying the analysis. Linear regression modelling is considered for experimental design.

2.3 Results and discussion

2.3.1 Transmission electron microscopy

TEM is an highly effective tool to evaluate quality of dispersion and characterize morphology of polymer blends both qualitatively and quantitatively. TEM images were taken on selected sample that contains untreated alumina nanofibers and vinyl silane treated alumina nanofibers used in this study. The results will be representative of all other samples since the same processing conditions were used. TEM images revealed agglomeration of untreated alumina nanofibers in polyester matrix at higher loading levels, whereas a decent quality of dispersion of nanofillers at lower loadings is observed as shown in Figure 2.9. It was observed that alumina nanofibers are retaining their fiber like morphology even after subjecting to high shear forces via three roll milling.

Although individual alumina nanofibers are visible, it is observed that the fibers are not completely de-bundled.

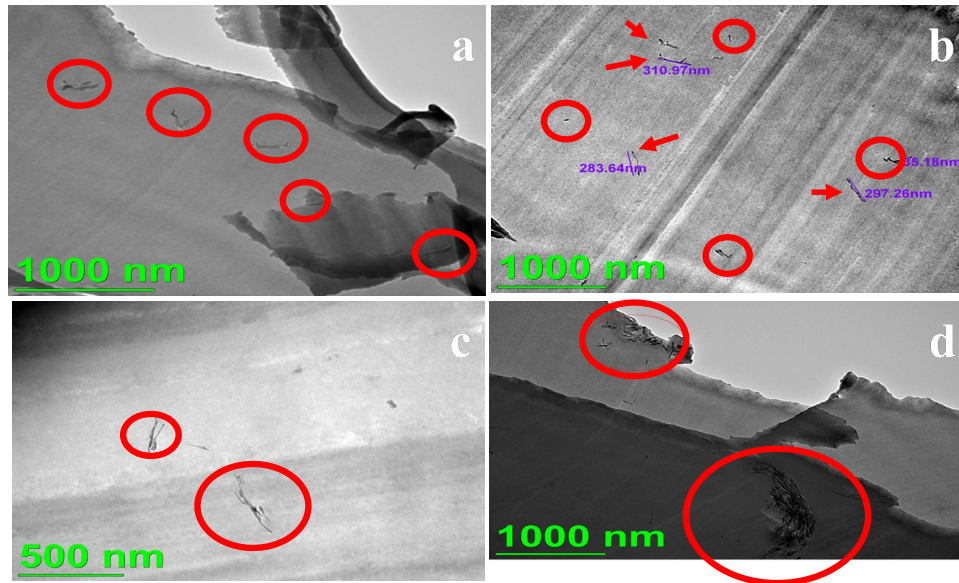


Figure 2.9: TEM images showing dispersion of (a) 25UT – Resin, (b) 50UT – Resin, (c) 75UT – Resin and (d) 100UT – Resin

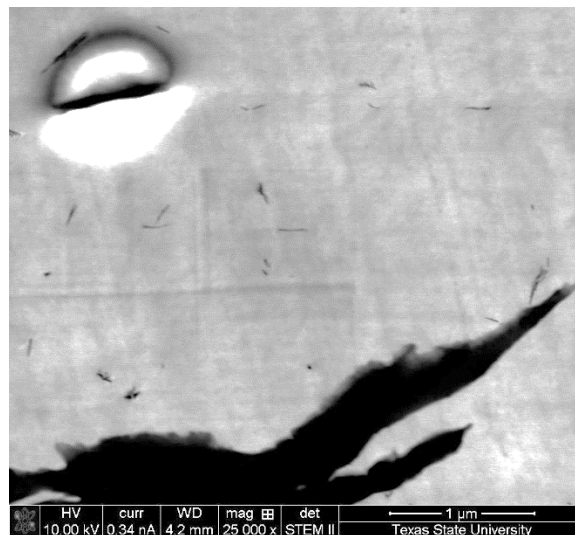


Figure 2.10: TEM image showing more uniform dispersion in VT - Resin.

Figure 2.10 shows effect of surface treatment on uniform dispersion, efficient debundling of alumina nanofibers as compared to untreated alumina nanofibers. It is worth mentioning that there exists alumina nanofiber clusters represented as black dots even after separation into long fibers, which are further reduced by vinyl silane treatment.

2.3.2 Refractive index

The refractive index measurement is ratio of velocity of light in vacuum to velocity of light in the polyester resin medium (Aghamollaei et al., 2019). The refractive index values showed consistency for respective loading levels as shown in Figure 2.11. The VT- Resin as compared to UT - Resin showed good refractive index values meaning that surface treatment of alumina nanofibers provided a good measure for homogenous dispersion. The refractive index values as compared to neat are very less indicating presence of alumina nanofibers, the decrease in values with increased loading levels is due to the light encountering alumina nanofibers and deflecting the light reducing index of refraction. Refractive index has dropped as ANF loading increased, but the max drop is about 0.06%. It indicates homogenous dispersion.

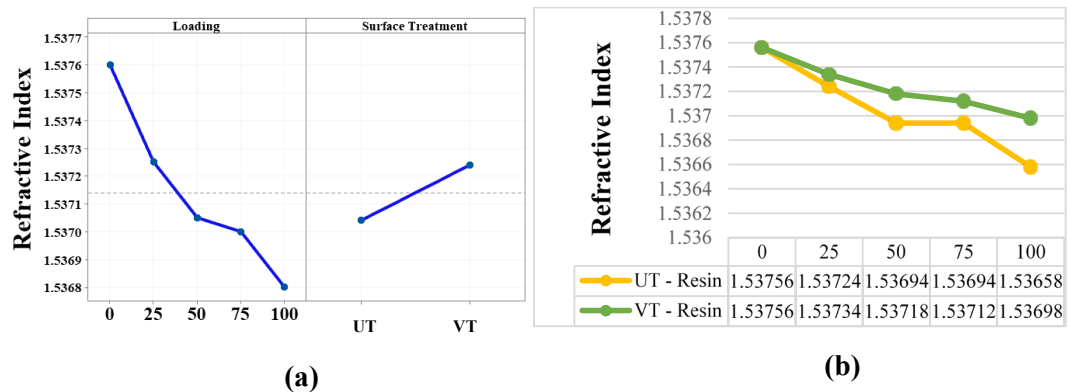


Figure 2.11: (a) Main effects plot and (b) interaction plot of refractive index values of UT and VT – Resin

2.3.3 Viscosity

The shear rate vs shear stress plots are given in Figure 2.12. The graphs of shear stress vs shear rate showed a linear relation, which means non-modified resin, shows a Newtonian behavior. A look at plots gives understanding of change in viscosity with increase in loading level of alumina nanofibers in polyester. The surface treatment of

alumina nanofibers helped in reducing the viscosity of polyester resin with respect to untreated alumina nanofiber modified polyester. It is evident from this plot that with surface treatment, lower viscosity of nanomodified polyester can be achieved and thus processing challenges can be addressed. Table 2.1 gives an understanding of viscosity changes with addition of nanoparticles and effect of surface treatment on viscosity property. It is quite evident that, surface treatment of alumina nanofibers has a positive effect on change in viscosity. The addition of surface functional groups reduces attraction among the nanoparticles thus increasing homogenous dispersion. For affordable processes such as vacuum assisted resin transfer molding (VARTM) or layup, the ideal viscosity range is 100-3000cP. When using vacuum assisted resin transfer molding, high viscosity of resin poses a challenge of increased time of resin infusion thus increasing fabrication time. In case of hand layup, high viscosity of resin increases air pockets during wetting of the fabrics. From the above result, a surface treatment of the nanoparticles can help reduce processing challenges associated with high viscosity. Figure 2.13 gives an understanding of main effects plot and interaction plot of variables. It was observed that increase in loading levels increased viscosity. However, the use of surface treatment reduced the viscosity.

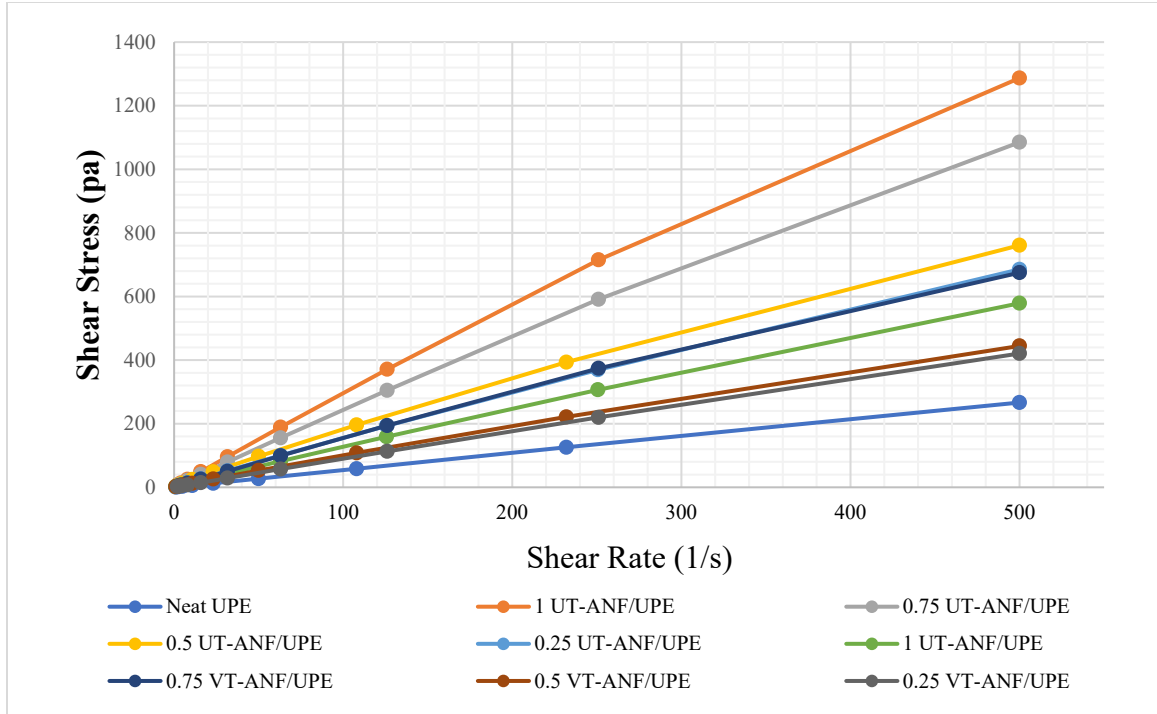


Figure 2.12: Summary of viscosity change of UT and VT – Resin

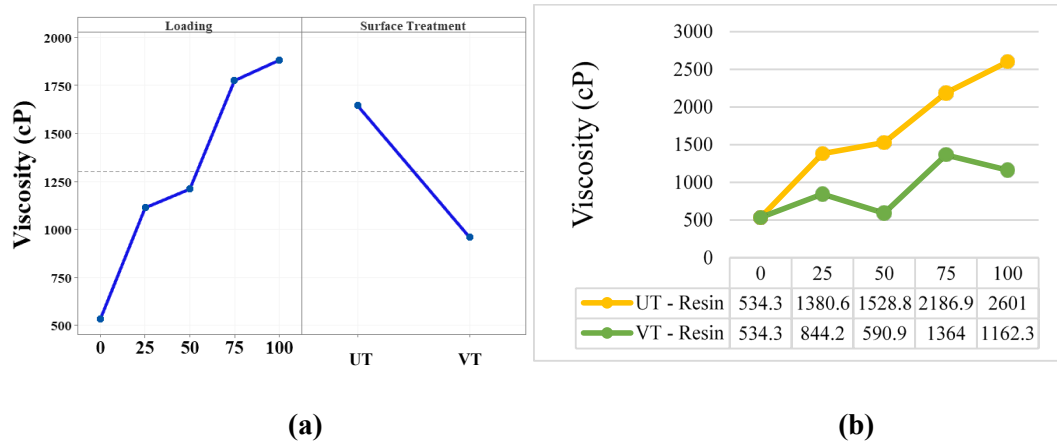


Figure 2.13: (a) Main effects plot and (b) interaction plot of viscosity values of UT and VT – Resin

2.3.4 Wettability

The degree to which liquids wet a fiber is a measure of bonding between fiber and resin, which results in efficient stress transfer between matrix and reinforcement. The contact angles measured provide information about wettability, essential in selecting or adjusting modifications on nanomaterial or fiber surfaces. The nanoparticle modification

of polyester resin changes surface energy of resin droplets when added onto substrate thus varying wettability. Surface treated alumina nanofibers during dispersion process broke down into smaller nanofibers providing continuous surface reducing surface energy and thus increasing wettability. The agglomerated lumps at higher concentration levels, creates a continuous rough surface thus by increasing the wetting angle. The results as depicted in Figure 2.14, shows that surface treatment of alumina nanofibers aids in more homogenous wetting with the matrix, thus positively contributing for efficient adhesion.

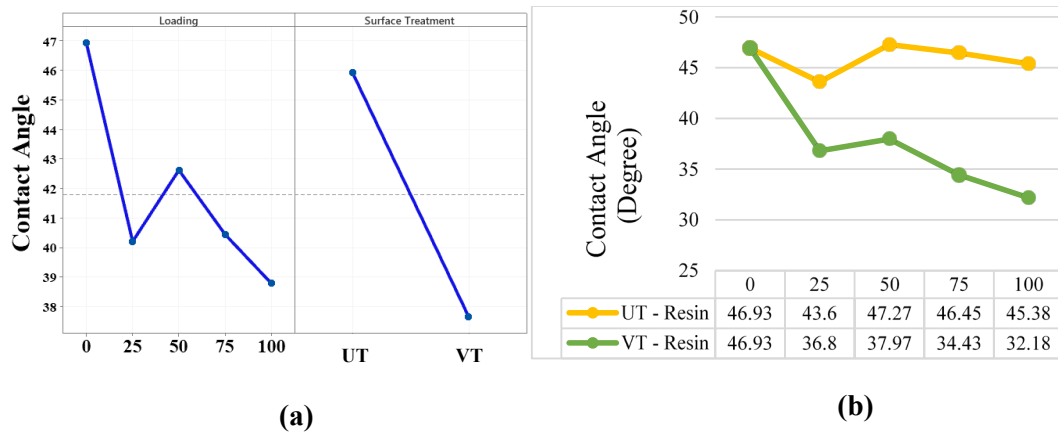


Figure 2.14: (a) Main effects plot and (b) interaction plot of contact angle values of UT and VT – Resin

Table 2.2: Experimental runs and results for physical properties

Runs	Loading	Surface Treatment	Refractive Index	Viscosity (cP)	Contact angle (θ)
1	0	0	1.53760	534.3	46.93
2	25	0	1.53724	1380.6	43.6
3	50	0	1.53694	1528.8	47.27
4	75	0	1.53694	2186.9	46.45
5	100	0	1.5366	2601	45.38
6	25	1	1.5373	844.2	36.8
7	50	1	1.5372	890.9	37.97
8	75	1	1.5371	1364	34.43
9	100	1	1.5370	1162.3	32.18

2.3.5 Mechanical properties

Table 2.3: Experimental runs and results for mechanical properties

Sample	Tensile Strength	Tensile Modulus	Equilibrium Toughness	Strain at Failure	Flexural Strength	Flexural Modulus	Izod Impact
	Mpa	Gpa	MJ/m ³	%	Mpa	Gpa	KJ/m ²
Resin	44.39	0.76	0.49	8.66	45.53	1.94	1.12
25UT – Resin	41.75	0.94	1.04	5.85	28.81	5.26	1.3
50UT – Resin	23.56	0.73	0.39	4.42	37.71	4.44	1.8
75UT – Resin	19.92	0.44	0.51	7.06	59.6	5.82	0.97
100UT – Resin	39.4	0.67	0.78	9.58	89.14	3.86	0.92
25VT - Resin	38.33	0.72	0.79	7.13	80.11	5.42	1.53
50VT – Resin	30.3	0.66	0.74	6.13	68.74	7.79	0.61
75VT – Resin	24.65	0.47	0.60	9.27	79.76	5.83	1.15
100VT - Resin	41.47	0.67	1.43	11.09	65.26	3.33	0.34

2.3.5.1 Tensile property

As observed in Figure 2.15, no significant improvement in tensile strength of UT – Resin and VT – Resin was observed, and main effects plot shows the results of regression analysis. The main effect of each factor on tensile strength is indicated in figure which notes that initial loss of tensile strength of polyester resin modified with alumina nanofibers until 0.75wt%. However, tensile strength regained 1wt%, although no significant improvement as compared to unmodified polyester resin. The influence of surface treatment can be observed with increase in tensile strengths. The result can be ascribed to better stress transfer of induced load from matrix and alumina nanofibers, which is further enhanced by surface treatment. The three-roll mill process induces high shearing forces as distance between rollers is decreased, which possibly dealt with efficient de-bundling of alumina nanofibers during each pass. However, it was observed from TEM images at higher loading levels, alumina nanofibers tend to agglomerate which is possibly due to high surface areas of nanofibers. Even though aspect ratio is

maintained, they tend to act as stress concentrators, which generally reduces properties. Conversely, drastic improvement in 1wt% loading as compared to lower loading levels alumina nanofiber modified polyester resin is observed even after agglomeration due to no surface treatment. The interaction plot indicates tensile strength response as an effect of predictors, loading level and surface treatment. The significance of interaction of alumina nanofiber concentration level and surface treatment is noted from the observation and for applications where resistance to tensile loading is prominent, higher loading levels might be helpful.

Like tensile strength response, tensile modulus as depicted in figure 2.16 showed decreasing trend with increasing loading level up to 0.75wt%. However, at 1wt% tensile modulus regained. Highest tensile modulus was recorded for 25UT – Resin in which the percentage improvement was 23.68%. The highest reduction in tensile modulus was recorded for 75UT – Resin and 75VT – Resin -42.11% and -38.11%/ The tensile modulus decreased with surface treatment. The interaction plot shows tensile modulus variation as a function of loading level and surface treatment. It was observed that surface treatment has no significant effect on response of modulus behavior. The tensile strength and tensile modulus of the material gives an understanding of maximum stress absorbed during elastic loading and stiffness, respectively. In general, a high tensile modulus means that material is rigid meaning materials shows elastic behavior under applied stress. In this study it was observed that addition of alumina nanofibers even after surface treatment have a negative effect on rigidity of material up to 0.75wt%. It was observed at loading level of 1wt% tensile modulus regained just as tensile strength.

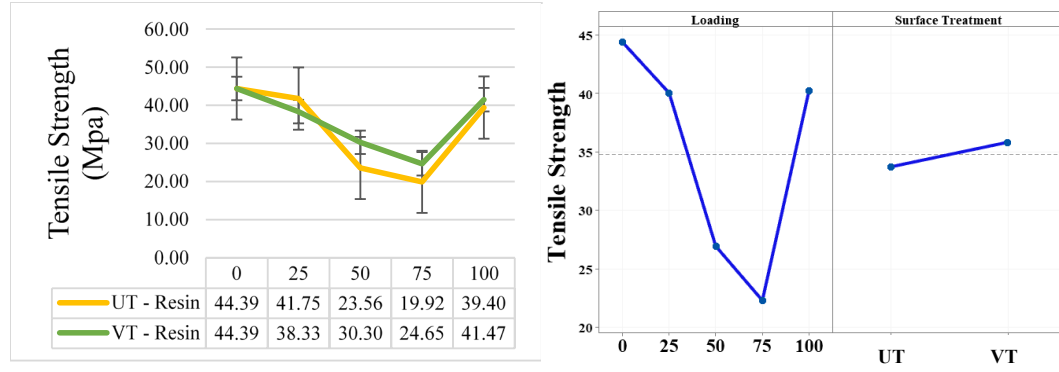


Figure 2.15: (a) Interaction plot and (b) main effects plot for tensile strength of UT and VT – Resin

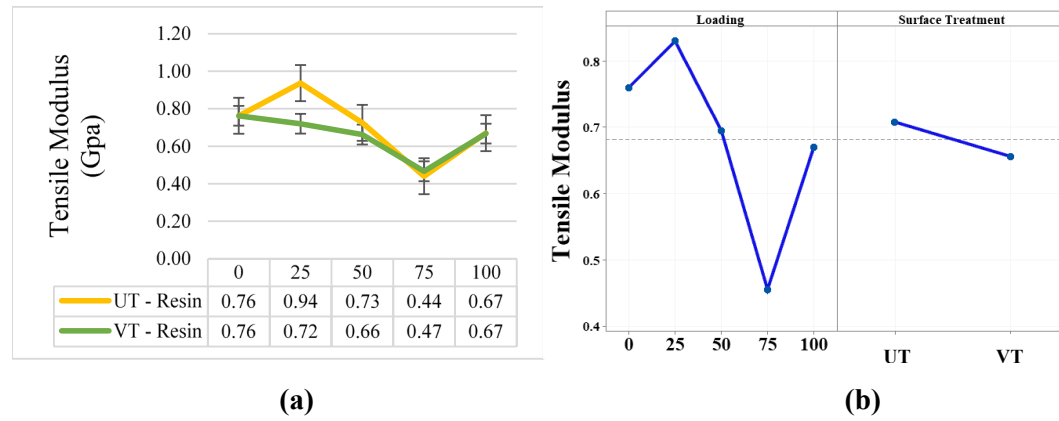


Figure 2.16: (a) Interaction plot and (b) main effects plot for tensile modulus of UT and VT – Resin

Equilibrium toughness is a measure of ability of a material to absorb energy before failure and is computed by integrating area under the curve of tensile stress and tensile strain from zero until maximum stress. It gives an understanding of total strain energy per unit volume induced by applied stress, which is beneficial in designing of composite systems. It was observed that 0.25wt% loading level of alumina nanofibers resulted in increased toughness, which was then reduced for further loadings. Although there is an improvement in energy absorption behavior of material with addition of alumina nanofibers (Figure 2.17), the surface treatment had a profound effect on

equilibrium toughness as observed in 100VT - Resin, which showed an improvement of 112%. Efficient bonding of alumina nanofibers to resin through surface treatment provided efficient stress transfer from resin to alumina nanofiber, requiring more energy absorption before failure. The strain at failure gives an indication of ductile or brittle property of polymer and it was observed that above 0.5wt% loading level, the alumina nanofiber imparted ductility to nanocomposite. High shear dispersion using three roll milling, resulted in the styrene evaporation. As the unsaturated polyester resin supplied by Interplastic corporation has 50% vinyl toluene and 50% styrene, most of diluent evaporation resulted in imparting ductility to specimens. But efficient dispersion and increased interaction between nanofiller and matrix, helped in regaining tensile properties. Unlike nanoparticles generally imparting rigidity to the matrix systems by increasing the crosslinking density, alumina nanofibers used in this study imparted results which are generally observed when using elastomers as the fillers for increased strain at failure and toughness.

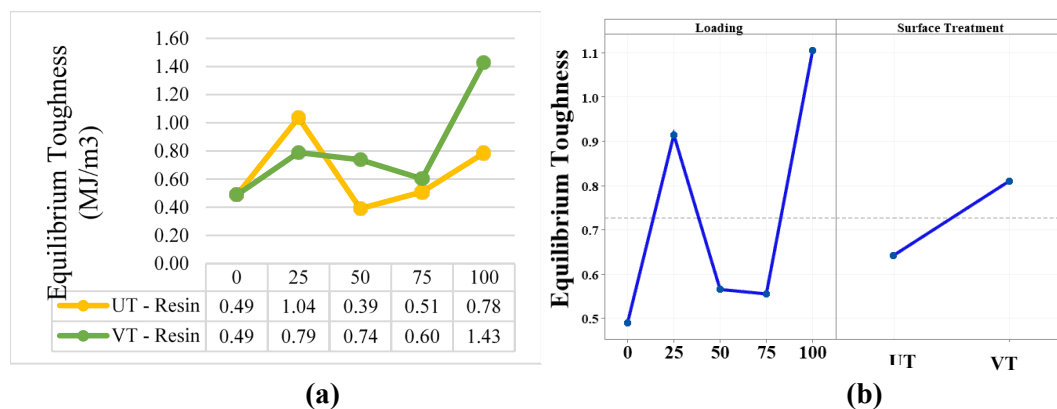


Figure 2.17: (a) Interaction plot and (b) main effects plot for equilibrium toughness of UT and VT – Resin

2.3.5.2 Flexure property

The flexure properties as shown in Figure 2.18, shows effect of nanoparticles in polyester resin. Due to unique fiber like morphology, alumina nanofibers could deflect cracks generated, thus causing increase in properties. A look at main effects plot revealed increase in flexure strength with increase in loading levels. However, an initial increase in flexure strength was observed for 0.25wt%, whereas further increase to 0.5wt% did not yield any improvement. Further loading levels of 0.75wt% and 1wt% has seen a rise in flexure strength property. The surface treatment of alumina nanofibers has proven to be effective in increasing in flexural strength and flexural modulus of polyester resin coupons. It is well known that increase in flexure strength and flexure modulus would result in higher toughness values, which is a result of difficulty of crack initiation and propagation within matrix. The interaction plot of two variables loading level and surface treatment reveals that surface treatment improves flexure property due to more surface area available to absorb energy and efficient crack deflection/crack pinning mechanisms. Surface treatment helped in enhancement in property at lower loading levels as can be observed from 25VT – Resin and 100UT – Resin percentage improvement. In view of increased viscosity at higher loading levels without any surface treatment as shown in figure resulting in processing difficulties and composite fabrication, it is worth mentioning that more prominent results can be attained at lower loadings with surface treatment.

The main effects plot and interaction plot for flexure modulus as a function of loading level and surface treatment are presented in Figure 2.19. Converse to flexure strength values observed, flexure modulus peaked for 50VT - Resin indicating role of

surface treatment on efficient stress transfer leading to improved property when compared to all other loading levels. The flexural modulus improved approximately by 301%. In contrast to above result, 50UT – Resin showed a drop in flexural modulus value. In comparison of alumina nanofiber modified polyester and neat polyester resin, ANF/UPE showed improved properties.

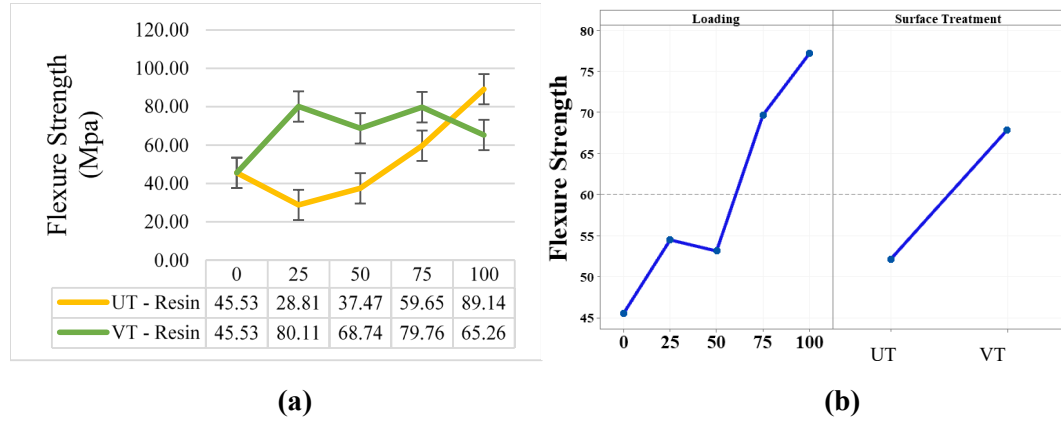


Figure 2.18: (a) Interaction plot and (b) main effects plot for flexure strength of UT and VT – Resin

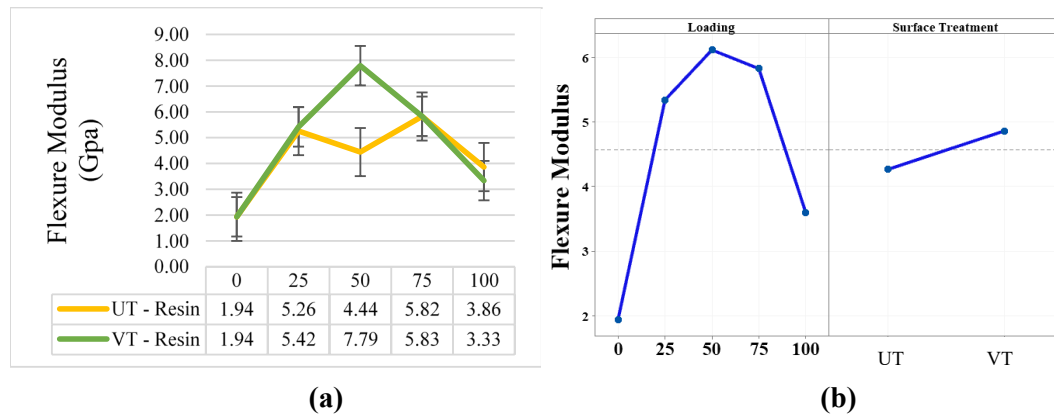


Figure 2.19: (a) Interaction plot and (b) main effects plot for flexure modulus of UT and VT – Resin

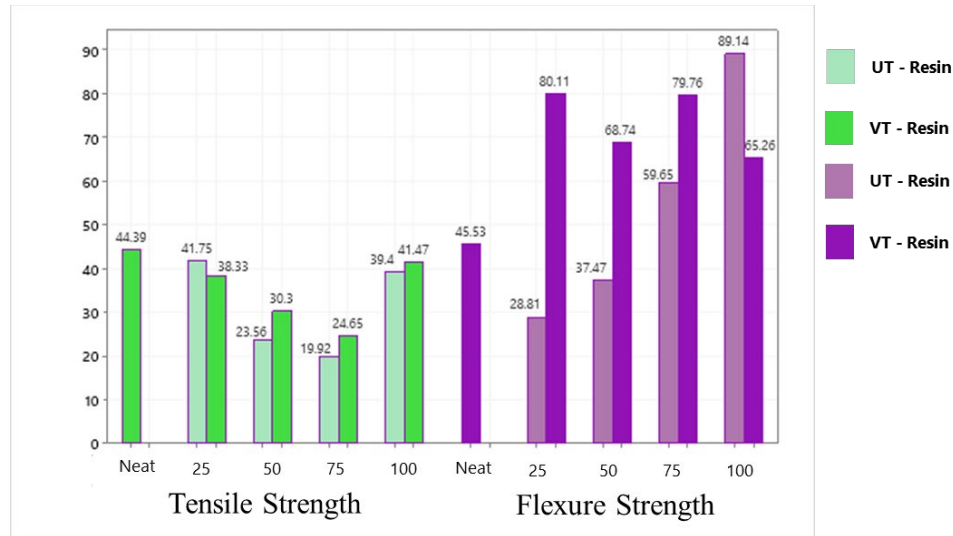


Figure 2.20: Comparison of tensile and flexure strength of UT and VT – Resin

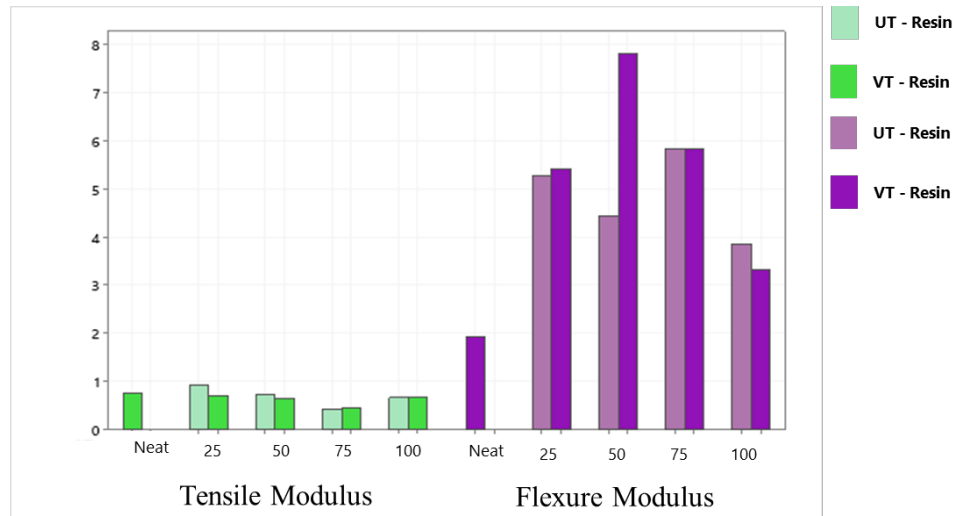


Figure 2.21: Comparison of tensile and flexure modulus of UT and VT - Resin

From Figure 2.20 and 2.21, it is observed that alumina nanofibers influenced flexure behavior significantly as compared to tensile behavior. The fiber like morphology of nanoparticles used in this study were able to resist out of plane loading rather than in plane loading. Although tensile strength and tensile modulus showed mixed results, it was observed that flexure properties are more pronounced. The high aspect ratio of alumina nanofibers provided improvement in flexural properties when compared to resin.

The effect of surface treatment is appreciable which lead to increased stiffness providing evidence of efficient bonding of matrix and alumina nanofiber, thus promoting efficient stress transfer. It is worth mentioning that surface treatment of alumina nanofibers, resulted in peak flexural properties at reduced concentration of nanofiller. From TEM images it can be noted that orientation of alumina nanofibers in polyester matrix is random. Since there is no alignment of nano fibers in loading direction during tensile testing created zones of higher stress concentrations leading to not significant improvement in tensile loading. The improvement in tensile properties at different loading levels is only result of good adhesion between alumina nanofiber and matrix. The primary function of matrix in a composite material, is to support efficient load transfer and prevent buckling of fibers under loading so that fibers take up more load resulting in improved properties. Considering alumina nanofibers as reinforcement in nanophase, due to random orientation of fibers, stress cracks developed during failure initiation deflect resulting in higher flexure properties. Hence, from results above, incorporation of alumina nanofibers might be a feasible solution in applications where out of plane properties are crucial.

2.3.5.3 Izod impact property

Unsaturated polyester resins due to their brittle nature generally possess inferior impact strength properties. However, introduction of micro and nano fillers to unsaturated polyester resin can improve its impact strength and impact toughness. The main effects plot and interaction plot of the izod impact strength with categorical predictors of loading level and surface treatment is shown in Figure 2.22. It was observed that influence of loading level of alumina nanofibers had no significance on izod impact

strength above 0.25wt%. Similarly, surface treatment had also a reducing effect on izod impact strength. The interaction plot showed that 25VT – Resin showed maximum impact strength in which improvement was 60.71%, whereas improvement in 25UT-Resin was 36.6%. Converse to regular understanding, surface treated alumina nanofibers at higher loading levels showed a decreasing trend in property. The behavior of nanoparticles in polymer matrix on mechanical properties is quite different from literature review presented in this study. The study suggests that depending on the morphology of nanoparticles (spherical, fiber and plate) the property prediction varies.

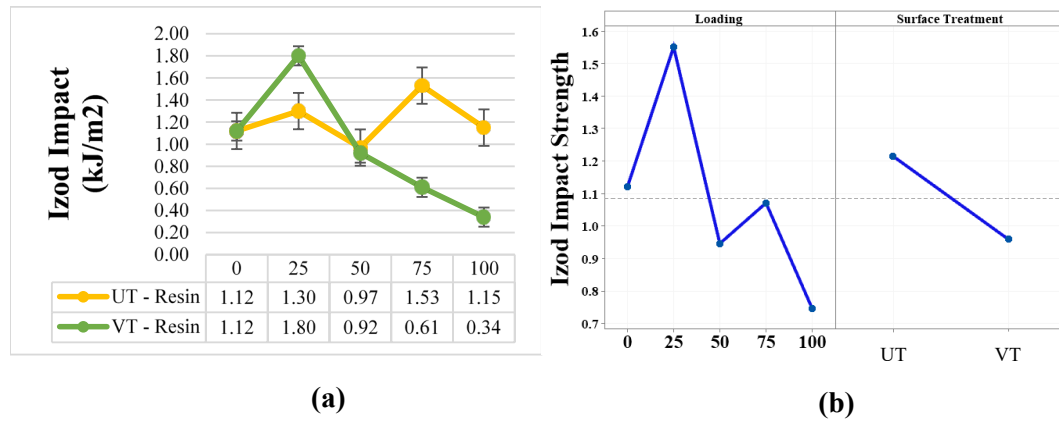


Figure 2.22: (a) Interaction plot and (b) main effects plot for izod impact of UT and VT – Resin

Table 2.4: Percentage improvement in properties for UT and VT – Resin

Sample	Tensile Strength	Tensile Modulus	Equilibrium Toughness	Strain at Failure	Flexure Strength	Flexure Modulus	Izod Impact
	MPa	GPa	MJ/m ³	%	MPa	GPa	KJ/m ²
Resin	-	-	-	-	-	-	-
25UT – Resin	-5.95	23.68	112.24	-32.45	-36.72	171.13	16.07
50UT – Resin	-46.92	-3.95	-20.41	-48.96	-17.70	12887	-13.39
75UT – Resin	-55.13	-42.11	22.45	7.04	31.01	200.00	36.61
100UT – Resin	-11.24	-11.84	59.18	10.62	95.78	98.97	2.68
25VT – Resin	-13.65	-5.26	61.22	-17.67	75.95	179.38	60.71
50VT – Resin	-3174	-13.16	51.02	-29.21	50.98	301.55	-17.86
75VT – Resin	-44.47	-38.16	22.45	7.04	75.18	200.52	-45.54
100VT - Resin	-6.58	-11.84	191.84	28.06	43.33	71.65	-69.64

Table 2.2 and Table 2.3 provide a summary of all test results and percentage improvement of properties as compared with neat samples tested.

2.4 Statistical analysis

There was a wide variation of test results obtained from nanofiller modification of polyester resin. To determine statistical significance of data we ran Analysis of Variance (ANOVA) using Minitab software to analyze changes in property. ANOVA was used keeping the confidence interval of 95%, indicating significant level of 0.05, to study significance of regression model and effect of each factor, interaction effects on measured response and to find significant factors. The computed statistical results (probability values) are compared to a significant level of confidence 0.05 to determine whether the observed data for factors considered were significant. In general, if probability value is less than or equal to 0.05, the null hypothesis is rejected, and alternate hypothesis is confirmed. Statistical analysis carried out include determination of each independent variable (alumina nanofiber) and two-way interactions (alumina nanofiber and surface treatment). The general regression linear model used for experimental design was:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \dots + \varepsilon \quad (1)$$

where y is the response, X_1 and X_2 are variables, β_0 is constant term, β_1 and β_2 are coefficients of polynomial for linear effects, β_{12} is the coefficient of polynomial for interaction effect and ε is the error. The response variables are limited to mechanical properties namely tensile strength, tensile modulus, equilibrium toughness, strain to failure, flexure strength, flexural modulus and izod impact strength in this study. The regression analysis presented here is the outcome of the factors (Alumina nanofibers,

surface treatment) and their interactions (alumina nanofibers and surface treatment) on the above considered responses. Table 2.4 presents general linear model with statistical significance for selected responses in combination with predictors. Generally, the positive sign in models has a positive effect on responses while a negative sign has a reducing effect. Table 2.5, 2.6 and 2.7 show coefficients of respective factors and P- values representing statistical significance of properties. The R^2 value shown in the ANOVA represented proportion of variance in response data explained by terms in the model. The difference between R^2 and R^2 (adj.) values implies the non-significant terms consisted in the model. The less difference between the R^2 and R^2 (adj.) indicates model was statistically significant and reliable to predict properties within the range of studies. Similarly, R^2 (pred.) values also give information about predictive ability of the model generated using regression analysis. All the mechanical properties showed less values for R^2 , R^2 (adj.) and R^2 (pred.) values meaning that models generated has less predictive ability on response as a function of predictors. However, the models generated for the physical properties as a function of predictive variables showed that the model generated has greater predictability. The high values of R^2 (adj.) and R^2 (pred.) showed greater dependence which prevent the probability error when a new term is introduced into the model.

Table 2.5: General linear regression model for each response

Response	Linear Models
Tensile Strength	$y = 40.17 - 12.7 (\text{wt}\%) - 0.4 (\text{ST}) + 4.9 (\text{wt}\% \times \text{ST})$
Tensile Modulus	$y = 0.844 - 0.272 (\text{wt}\%) - 0.102 (\text{ST}) + 0.100 (\text{wt}\% \times \text{ST})$
Equilibrium Toughness	$y = 0.632 + 0.020 (\text{wt}\%) - 0.160 (\text{ST}) + 0.656 (\text{wt}\% \times \text{ST})$
Strain at failure	$y = 6.50 + 1.22 (\text{wt}\%) + 0.55 (\text{ST}) + 1.58 (\text{wt}\% \times \text{ST})$
Flexure Strength	$y = 28.5 + 47.2 (\text{wt}\%) + 31.5 (\text{ST}) - 31.6 (\text{wt}\% \times \text{ST})$
Flexure Modulus	$y = 3.38 + 1.76 (\text{wt}\%) + 0.84 (\text{ST}) - 0.48 (\text{wt}\% \times \text{ST})$
Izod Impact Strength	$y = 1.156 + 0.116 (\text{wt}\%) + 0.352 (\text{ST}) - 1.216 (\text{wt}\% \times \text{ST})$

Table 2.6: Summary of analysis of variance for tensile properties

Term	Tensile Strength		Tensile Modulus		Equil. Toughness		Strain at Failure	
	Coef	P-Value	Coef	P-Value	Coef	P-Value	Coef	P-Value
Constant	40.17	0.002	0.844	0.000	0.632	0.034	6.50	0.007
Wt%	-12.7	0.365	-0.272	0.172	0.020	0.959	1.22	0.661
ST	-0.4	0.970	-0.102	0.527	-0.160	0.641	0.55	0.818
Wt% x ST	4.9	0.798	0.100	0.701	0.656	0.264	1.58	0.688
R ²	19.14		38.28		40.13		28.20	
R ² (adj.)	0.00		7.42		10.19		0.00	
R ² (pred.)	0.00		0.00		0.00		0.00	

Table 2.7: Summary of analysis of variance for flexure and izod properties

Term	Flexure Strength		Flexure Modulus		Izod Impact	
	Coef	P-Value	Coef	P-Value	Coef	P-Value
Constant	28.5	0.058	3.38	0.084	1.156	0.004
Wt%	47.2	0.055	1.76	0.534	0.116	0.791
ST	31.5	0.116	0.84	0.729	0.352	0.368
Wt% x ST	-31.6	0.304	-0.48	0.902	-1.216	0.085
R ²	59.43		12.57		58.56	
R ² (adj.)	39.15		0.00		37.97	
R ² (pred.)	0.00		0.00		0.00	

Table 2.8: Summary of analysis of variance for physical properties

Term	Refractive Index		Viscosity		Contact Angle	
	Coef	P-Value	Coef	P-Value	Coef	P-Value
Constant	1.53750	0.000	658	0.002	45.98	0.000
Wt%	-0.000904	0.000	1976	0.000	-0.10	0.975
ST	0.000008	0.930	-54	0.780	-1.94	0.488
Wt% x ST	0.000352	0.048	-1266	0.006	-12.65	0.026
R ²	95.39		95.79		88.77	
R ² (adj.)	93.08		93.69		83.15	
R ² (pred.)	88.31		87.08		63.21	

The normal probability plots give information about reliability of the ANOVA results. If the data points fall near the straight line, it is safe to say that the data are reliable. The residuals as indicated in Figure 2.23 for all mechanical responses are close to straight line indicating the normal distribution of data points. The same was observed for physical properties as observed in Figure 2.24.

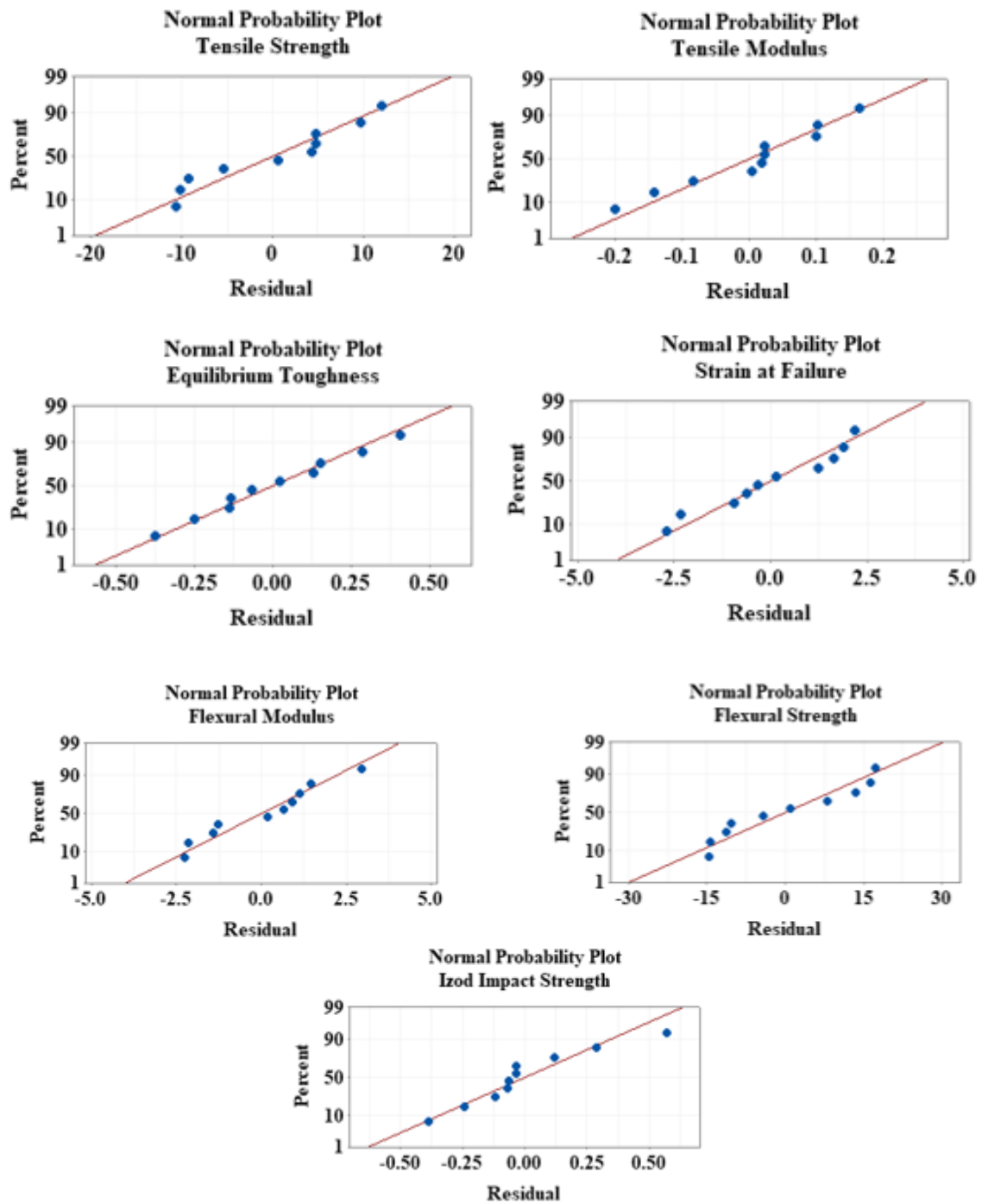


Figure 2.23: Normal probability plot of mechanical properties of UT and VT - Resin

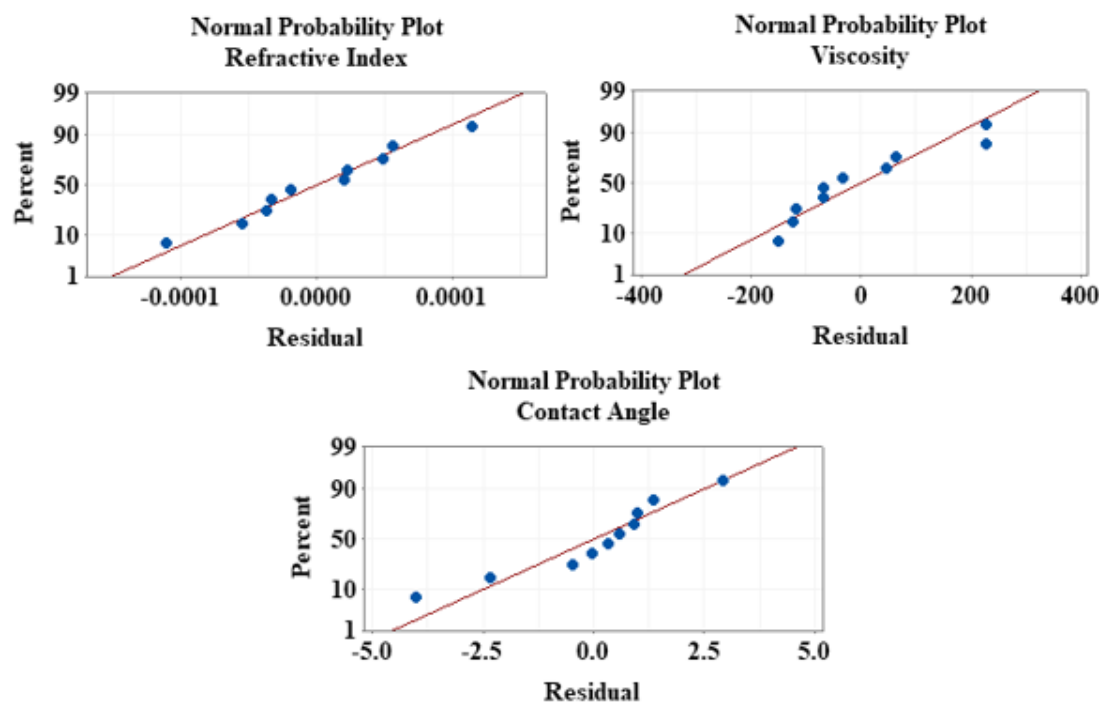


Fig 2.24: Normal probability plots of physical properties of UT and VT – Resin

The goal of regression analysis is to find values of parameters that fit the model accurately. Linear regression modelling fits a straight-line to the data and it was observed from statistical analysis that linear modelling does not do justification in analyzing the significance. A non-linear regression will enhance the idea to fit data accurately and need to be considered for future analysis.

2.5 Conclusions

Transmission electron microscopy, viscosity, wettability, refractive index, tensile, flexure and izod impact property of polyester coupons modified with untreated alumina nanofibers and surface treated alumina nanofibers is studied and compared. TEM images showed agglomeration but decent dispersion at higher loading levels. As expected, viscosity increased with loading level of alumina nanofibers. Surface treatment has proven effective to impart mechanical properties at reduced viscosity. The refractive

index also proves efficiency of surface treatment of alumina nanofibers in promoting homogenous dispersion into polyester resin.

1. The viscosity rise observed was not substantial in polyester modified with surface treated alumina nanofibers. At 0.25wt% loading level, viscosity rise in VT - Resin was 58% as opposed to 158% at same loading level of UT - Resin. Viscosity is an important factor in affordable processes, as it effects the quality of composite by including unnecessary voids, leading to inferior mechanical properties. For affordable processes such as VARTM or layup, the viscosity range of 100-1000cP is ideal for better quality.
2. Regardless of surface treatment of alumina nanofibers, major of the mechanical properties showed good improvement at 0.25wt% loading level.
3. The equilibrium toughness, which is an important parameter against deformation, has seen an improvement of 112.2% for 25UT - Resin. With surface treatment at 1wt% loading level has seen a maximum improvement of 191.8%.
4. Flexural properties have improved with addition of alumina nanofibers. However, with surface treatment it was observed that 0.25wt% loading level strength improved by 43.3%.
5. Izod impact property for 25VT - Resin has seen maximum improvement by 60.7%.
6. When tensile properties are desired in composite material, the surface treatment or incorporation of alumina nanofibers do not provide positive effects at lower loading levels.

7. The out of plane property tests flexure and izod impact are enhanced by addition of surface treatment at 0.25wt% concentration level.
8. It can be concluded from this study that inclusion of alumina nanofibers has shown high potential of improving mechanical properties. It is validated that surface treatment of alumina nanofibers has potential to improve properties significantly at lower loading levels. Selection of low loading levels is important to tackle processing challenges and less defects into composites.
9. For each response, a model is provided with their adequacy investigated, based on experimental data. - The linear regression model did not show good fit or good accuracy based on the R^2 , R^2 (adj.) and R^2 (pred.) values, Choosing the best nonlinear functions that expect or describes the relationship of response and predictors is imperative to assess significance of test data.
10. It is imperative to consider using different silane coupling agents compatible with polyester and alumina nanofibers to evaluate their effects on mechanical properties at reduced viscosity and homogenous dispersion.

3. GLASS FIBER REINFORCED ALUMINA NANOFIBER FILLED POLYESTER COMPOSITES: MANUFACTURING AND PERFORMANCE EVALUATION

Glass fiber composites have become cost-effective solution in industrial composite market against high cost carbon fiber composites which are limited to aerospace applications. Unsaturated polyester resin infused glass fiber composite due to its good mechanical performance and low cost have gained prominence. Glass fiber reinforced polymer nanocomposites have been researched for a variety of applications that require impact resistance, flame retardancy, and improved fatigue performance. Research utilizing different nanoparticles to enhance mechanical properties have been of focus in designing for improved fracture toughness. Addition of nanoparticles to these composites have proven to be more effective in enhancing mechanical performance without drastically increasing the cost. Ionic and covalent bonding characteristic of ceramic nanoparticles offers good thermal conductivity, electrical resistivity, and low dielectric constant. Nanoscale precipitation and point defects introduction through incorporation of nanoparticles can provide excellent thermal insulation properties which find applications in subsea, construction and piping industry (Papadopoulos, 2005; Wang, Zhang, & Tang, 2012). The nano-porosity and electrostatic attraction offered by alumina nanofibers with high surface areas is seen as a great potential for water treatment to reduce contaminants through adsorption. Alumina nanofibers can find applications where high thermal stability is desired. The high thermal stability often can lead to improved fire resistance and char formation offering thermal protection to composites at affordable cost.

The objective of the study is to evaluate mechanical performance of alumina nanofiber modification of unsaturated polyester reinforced with woven E-glass fibers. 0/90 woven E-Glass fabric from Owens corning having GSM 888.0 was selected as reinforcement and unsaturated polyester resin SIL47DA-2949 with a viscosity of 396 cP from Interplastic Corporation as matrix. 1-D capillary system air gel structure ensures uniform distribution of alumina nanofibers due to sufficient inter fiber distance. Alumina nanofibers with minimal aspect ratio 18-20 under trade name NafenTM from ANF Technology are used as nanofillers. In addition to low density and fiber morphology which offers benefits of tailoring the aspect ratio, it has been considered economical than other forms of ceramic nanoparticles in terms of manufacturability and monetary cost. One set of composites were modified with untreated alumina nanofibers and the second set were modified with vinyl silane coupling (organic content 6-7%) agent treated alumina nanofibers. For a uniform distribution in polymer matrix, better wettability and interaction, the surface energy of fiber should be close to surface energy of polymer. Loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% were used for both sets of composites laminates. The glass polyester composites modified with untreated alumina nanofibers are here from referred to as - UT - Composite and composites modified with vinyl silane treated alumina nanofibers as VT - Composite. Benzoyl Peroxide acquired from Sigma-Aldrich is used as curing agent with external simulator.

3.1 Processing

3.1.1 Dispersion of nanoparticles

Dispersion of alumina nanofibers at required concentration levels into unsaturated polyester resin was done by three roll mill apparatus manufactured by EXAKT

technologies. The three adjacent cylindrical rolls each turning at different velocities, result in pure shear providing efficient means to de-bundle nanoparticle agglomerates. The mill is equipped with electronic speed control and provision to set the gap between rollers during operation. The gap between the rollers is set at 25 μ m, 15 μ m and 7.5 μ m respectively for three passes. After dispersion of nanofillers according to chosen loading levels into polyester resin, benzoyl peroxide was added to nanomodified unsaturated polyester in the proportion of 1phr. High shear mixing results in air entrapment, thus needing degassing. Once after dispersion, the mixture is placed in degassing chamber (Figure 3.1). The chamber was maintained at a vacuum of approximately 5-10 torr, aiding in removal of all the entrapped air or gases out of the resin. This step ensures that no excessive voids are present in final composite laminate resulting in high quality final product. Time duration for degassing was selected to be 15-30min to ensure there is no loss of styrene which would otherwise lead to undesired properties and void formation.

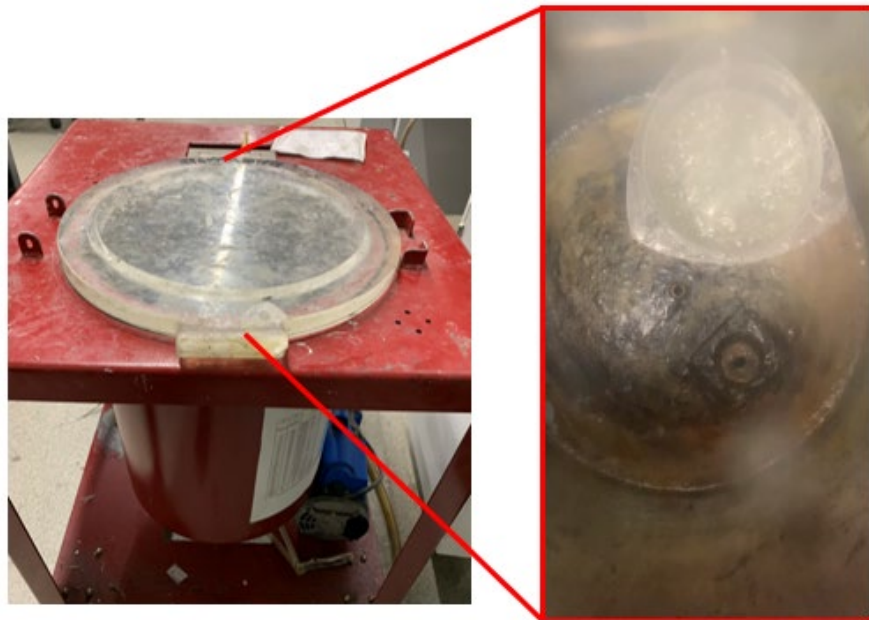


Figure 3.1: Degassing of nanomodified resin.

3.1.2 Fabrication of composite laminates

Hand layup or often referred to as wet layup, autoclave processing, filament winding, resin transfer molding (RTM), vacuum assisted resin transfer molding (VARTM) are among different types of manufacturing process available for composite laminate fabrication. In VARTM process, where impregnation is aided by pulling out vacuum, volatile content formation and nanoparticle filtration is seen as a major issue. In a typical hand layup process, layers of reinforcement are cut to required shapes and are placed on surface molds which are treated with release agent. Each layer of reinforcement is applied with thermoset resin matrix and are pressured with use of rollers to ensure proper adhesion between matrix and the reinforcement, also removing entrapped air bubbles. Depending on requirement of laminate thickness, number of layers of reinforcement is applied. The schematic of hand layup is as shown in Figure 3.2 below. The steps in traditional hand layup process consists of i. Mold preparation, ii. Matrix application to dry fabric, iii. Layup of fabric to achieve desired thickness, iv. Curing of laminate (green cure or curing with the aid of external factor). Although hand layup process ensures reinforcement control and removing of excess resin providing a means to control fiber volume fraction, the process exhibits unwanted results in terms of inferior mechanical properties through introduction of voids.

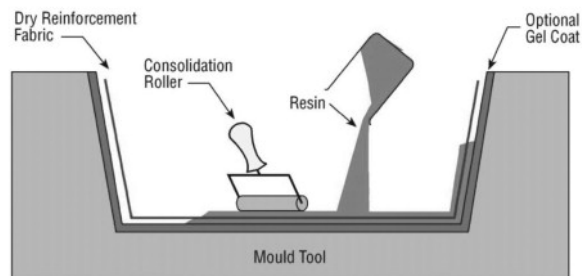


Figure 3.2: Illustration of layup process for composite fabrication

In the present research, instead of a traditional hand layup approach, double drip resin bath donated to Advanced Composite Laboratory by Hexcel Corporation, Seguin, Texas is used for impregnation. The double drip resin bath as shown in Figure 3.3 consist of a provision for resin matrix and a set of rollers which squeeze out the excess resin when pulling fabric through the equipment. Fiber matrix adhesion is critical in processing and performance of composites. Fiber matrix debonding eventually leading to delamination is an important damage mechanism in composites under loading. Use of double drip resin bath ensured uniform wetting of fabric which is crucial in eliminating dry spots and voids. After pulling fabric through resin bath, the layers are stacked depending on thickness requirement and is then transferred for final curing into hydraulic compression press. The final cured laminates are then post cured at 110⁰C for three hours in the programmable oven.

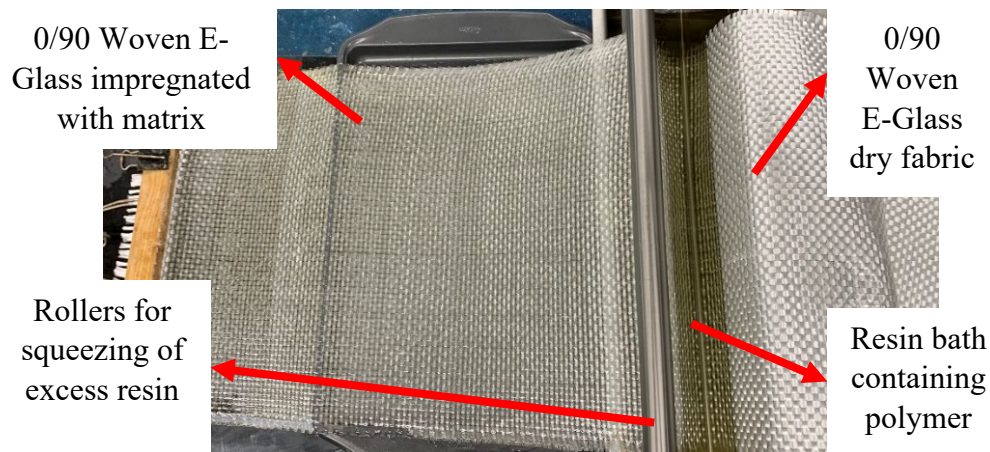


Figure 3.3: Double drip pan and wetting of fabric.

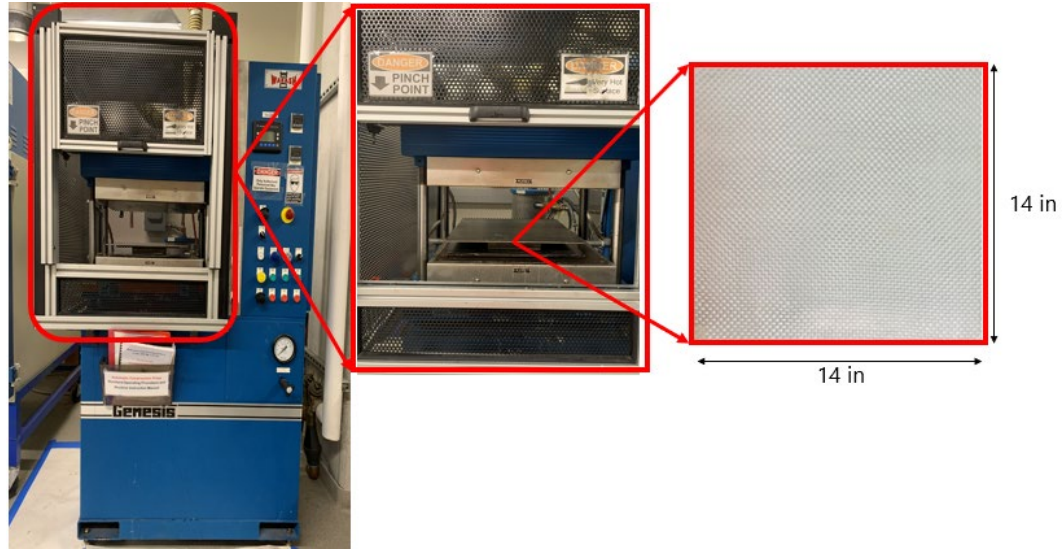


Figure 3.4: Wabash hydraulic press for compression molding (14in x 14in).

3.2 Fiber volume fraction

The major disadvantage of using layup process is it induces voids in final composite material and the addition of nanoparticles can worsen quality since polymerization is affected by nanofillers. It is of high importance to assess fiber volume fraction of final laminate, since the percentage of load bearing fiber content has a direct effect on mechanical properties. Higher void content usually means greater susceptibility to moisture absorption and weathering and increased variation or scatter in strength properties.

The fiber volume fraction was obtained using ASTM D3171 standard, which specifies use of one sample, having a cuboid shape with minimum surface area of 625mm^2 . The sample was conditioned at 25°C , at a relative humidity of 50% using procedure G from the standard. The density of 1 in x 1 in x 't' specimen is determined according to ASTM D792 standard. The specimen is then placed in a desiccated crucible and is then placed in the muffle furnace. The furnace is then heated up to 650°C for 6h. The furnace is cooled to room temperature after the cycle and weight of specimen in its

holder is recorded. At the specified temperature, polyester matrix is completely combusted, leaving reinforcement/residue. Using the equations specified below, constituent material contents in composite are calculated.

Fiber volume fraction

$$V_f = \left(\frac{M_f}{M_i} \right) \times 100 \times \frac{\rho_c}{\rho_f}$$

Matrix volume fraction

$$V_m = \left(\frac{M_i - M_f}{M_i} \right) \times 100 \times \frac{\rho_c}{\rho_m}$$

Void volume fraction

$$V_v = 100 - (V_f + V_m)$$

M_i = Initial mass of specimen, grams

M_f = Final mass of specimen after combustion, grams

ρ_c = Density of composite specimen, g/cc

ρ_f = Density of reinforcement, g/cc

ρ_m = Density of matrix, g/cc

The overall constituent volume fractions are given in Table 3.1. It was observed that increase in void content is observed with addition of alumina nanofibers. Though there is an increase in void content with surface treated alumina nanofiber modification, the void content is less as compared to untreated alumina nanofiber modification. The samples tested in this category for fiber volume and void volume fraction consisted of six layers of woven glass fabric used for static testing and is an average of five test samples used for mechanical testing.

Table 3.1: Overall constituent volume fractions in UT and VT – Composite

Sample	Density	Fiber Volume Fraction	Matrix Volume Fraction	Void Volume Fraction
	g/cc	V_f	V_m	V_v
Composite	1.98	57	41.9	1.1
25UT – Composite	2.00	60.7	36.2	3.1
50UT - Composite	1.98	61.4	32.9	5.7
75UT – Composite	2.02	65.8	27.6	6.6
100UT – Composite	2.00	65.8	25.8	8.4
25VT – Composite	2.01	60.7	36.9	2.4
50VT – Composite	2.02	63.8	31.8	4.4
75VT – Composite	2.04	65.8	28.9	5.3
100VT - Composite	2.00	64.8	27.9	7.3

3.3 Characterization

3.3.1 Mechanical testing

There are several in plane and out of plane tests available to evaluate a material for its overall performance depending on the constituent properties chosen. The static tests chosen to evaluate the behavior of alumina nanofiber modified composites in this study include tensile test, flexure test and interlaminar shear test. Since, the end application targeted for composites being studied in this research are geared towards impact strength and toughness enhancement, static tests which could simulate impact scenario are chosen. Based on energy absorption behavior of laminates subjected to impact provided in chapter 1, primary failure mode is delamination. Flexure test and Interlaminar shear testing are class of tests which simulate material behavior to out-of-plane loading. The interfacial strengths restricting debonding and delamination can be easily assessed using these tests and might provide an understanding to study behavior under impact loading.

3.3.1.1 Tensile test

The static tensile testing was performed on woven glass reinforced untreated and vinyl silane treated alumina nanofiber modified polyester composites using MTS 810 Servo Hydraulic System. The tests were according to ASTM D3039 standard which specifies a sample size of 10 in x 1 in x t'. The tensile test was conducted in displacement control mode with a cross head rate of 2mm/min. Ultimate tensile strength, strain at failure, Youngs modulus and equilibrium toughness were evaluated as an average of five samples. The equations used for calculating above properties are provided below. The equilibrium toughness is computed by using area under the stress-strain curve and is calculated by integrating the curve from limits zero to maximum stress before failure.

Tensile Strength

$$F^{tu} = P^{max} / A$$

$$\sigma_i = P_i / A$$

F^{tu} = Ultimate tensile strength, MPa.

P^{max} = Maximum force before failure, N.

σ_i = Tensile stress at ith data point, MPa.

P_i = Force at ith data point, N.

A = Average cross-sectional area of the specimen.

Tensile Strain

$$\epsilon_i = \delta_i / L_g$$

ϵ_i = Tensile strain at ith data point.

δ_i = Extensometer displacement at ith data point.

L_g = Extensometer gage length, mm.

Modulus of Elasticity

$$E = \delta\sigma / \delta\epsilon$$

$\delta\sigma$ = difference in applied stress between two strain points.

$\delta\epsilon$ = difference between two strain points.

3.3.1.2 Flexure test

The flexure testing was performed on woven glass reinforced untreated and surface treated alumina nanofiber modified polyester composites using MTS 810 Servo Hydraulic System. The tests were according to ASTM D7264 standard which specifies a sample size of 5.5 in x 0.5 in x 't' and a span to thickness ratio of 32:1 was selected based on standard. The flexure test was conducted in displacement control mode with a cross head rate of 1mm.min⁻¹. Flexure strength, Flexure modulus were evaluated as an average of five samples.

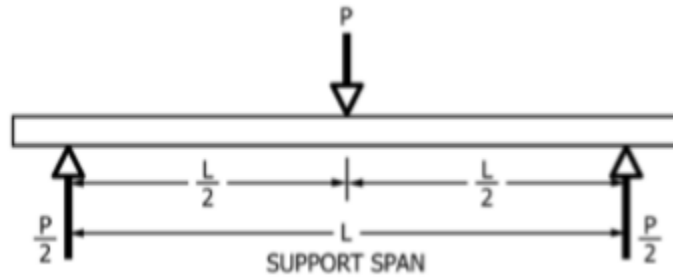


Figure 3.5: ASTM D7264 three-point bend test loading diagram

3.3.1.3 Short beam shear test

The short beam shear test was performed on woven glass reinforced untreated and vinyl silane treated alumina nanofiber modified polyester composites using MTS 810 Servo Hydraulic System. The tests were according to ASTM D2344 standard which specifies a sample size of 6't' x 2't' x 't'. The length-to-specimen thickness ratio of 4.0 was used. Interlaminar shear strength was evaluated as an average of five samples.

Short Beam Strength

$$F^{sbs} = 0.75 \times (P_m / A)$$

F^{sbs} = short beam strength, MPa

P_m = Maximum load observed during test, N

A = measured specimen width (b) x measured specimen thickness (t)

3.3.1.4 Scanning electron microscopy

SEM imaging was performed using Helios Nano lab 400 to analyze failure modes at 10.0kV and a current range between 0.69amp and 2.7amp. The samples were previously treated with EMS150T ES sputter coater to add a layer of carbon of at least 20nm.



Figure 3.6: EMS 150T Sputter coater and Helios Nanolab 400 for SEM Studies

3.4 Results and discussion

3.4.1 Static mechanical properties

Table 3.3: Static mechanical test results of UT and VT - Composite

Tests	Composite	25		50		75		100	
		UT	VT	UT	VT	UT	VT	UT	VT
Tensile Strength (MPa)	410.82 (28.51)	521.32 (19.11)	507.45 (11.88)	506.25 (14.88)	508.23 (8.18)	453.18 (16.02)	520.35 (0.223)	524.60 (5.56)	520.44 (7.26)
Tensile Modulus (GPa)	18.62 (2.86)	20.64 (0.54)	22.69 (1.51)	17.52 (0.64)	25.25 (2.29)	18.87 (1.41)	23.24 (1.92)	21.78 (0.32)	24.88 (1.57)
% Elongation	6.72 (0.50)	4.96 (0.41)	3.03 (0.79)	4.09 (0.18)	2.90 (1.08)	4.63 (0.22)	1.86 (0.14)	5.43 (0.73)	5.50 (1.98)
Equilibrium Toughness (MJ/m ³)	7.08	10.29	10.22	10.02	10.07	8.70	10.44	10.24	9.95
Flexure Strength (MPa)	112.52 (17.14)	117.11 (14.91)	126.18 (13.05)	93.67 (3.44)	119.45 (3.10)	115.51 (12.86)	121.60 (12.25)	133.53 (14.87)	129.69 (3.47)
Flexure Modulus (GPa)	22.82 (7.59)	24.46 (2.36)	28.02 (4.98)	21.25 (1.05)	26.20 (1.88)	23.21 (1.51)	27.98 (4.05)	29.24 (1.56)	30.98 (2.79)
Short Beam Strength (MPa)	12.61 (0.85)	13.40 (1.29)	14.93 (2.84)	10.45 (0.85)	11.94 (1.08)	12.69 (2.16)	10.72 (1.85)	10.66 (1.37)	13.68 (2.63)

(Standard deviations are in parenthesis)

Table 3.4: Percentage improvement in static properties of UT and VT - Composite

Tests	Composite	25		50		75		100	
		UT	VT	UT	VT	UT	VT	UT	VT
Tensile Strength	-	26.9	23.5	23.2	23.7	10.3	26.7	27.7	26.9
Tensile Modulus	-	10.8	21.9	-5.9	35.6	1.3	24.8	16.9	33.6
% Elongation	-	-26.2	-54.9	-39.1	-56.8	-31.1	-72.3	-19.2	-18.2
Equilibrium Toughness	-	45.3	44.5	41.5	42.2	22.9	47.7	44.6	40.5
Flexure Strength	-	4.1	12.1	-16.5	6.2	2.7	8.1	18.7	15.3
Flexure Modulus	-	7.2	22.8	-6.9	14.8	1.7	22.6	28.1	35.8
Short Beam Strength	-	6.3	18.4	-17.1	-5.3	0.6	-15.0	-15.5	8.5

3.4.1.1 Tensile property

As observed in Figure 3.7, which shows main effects plot and interaction plot of the predictors on tensile response, tensile strength of composites increased drastically with addition of alumina nanofibers. The increase in tensile strength is more pronounced with surface treatment of alumina nanofibers using vinyl silane coupling agent. The interaction plot provides an understanding of effect of alumina nanofibers and surface treatment on tensile strength properties. It was observed that at 0.25wt% loading level of ANF without any surface treatment, tensile strength recorded a higher value. Though there was a decrease in tensile strength until 0.75wt%, strength regained at 1wt%. As for VT - Composite after attaining maximum strength at 0.25wt%, there was no significant increase in strength and all through strength values seemed to be constant.

The tensile modulus values seemed to be affected by surface treatment of alumina nanofibers. The VT - Composites exhibited increased tensile modulus. The interaction plot shows tensile modulus variation as a function of loading level and surface treatment. It was observed that surface treatment has a significant effect on response of modulus behavior. The tensile strength and tensile modulus of material gives an understanding of maximum stress absorbed during elastic loading and stiffness, respectively. In general, a high tensile modulus means that material is rigid meaning materials shows elastic behavior under applied stress. In this study it was observed that addition of alumina nanofibers after surface treatment has positive effect on rigidity of VT - Composite when compared to UT - Composite. It was observed that with increasing loading level to 1wt% tensile modulus regained just as tensile strength.

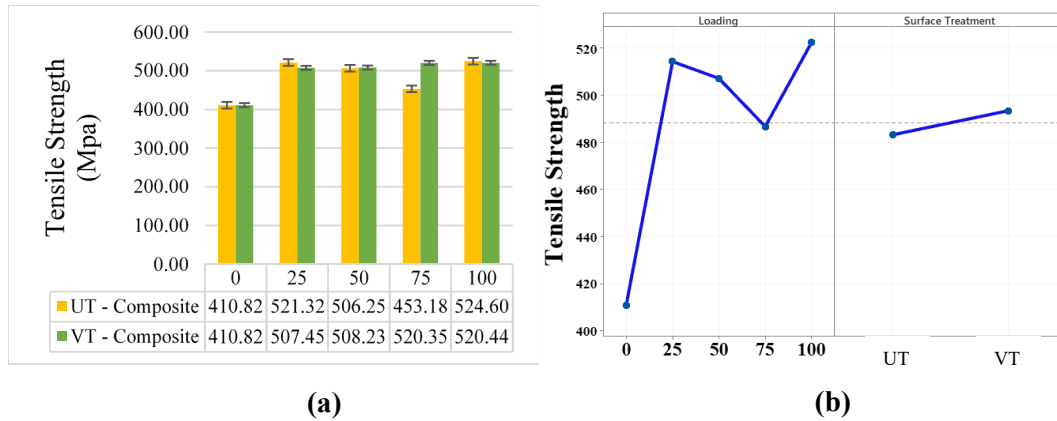


Figure 3.7: (a) Interaction plot and (b) main effects plot for tensile strength of UT and VT – Composite

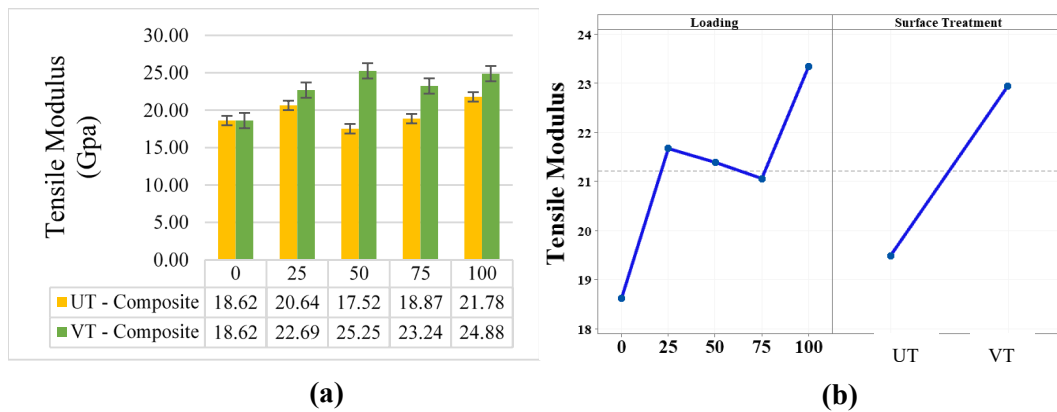


Figure 3.8: (a) Interaction plot and (b) main effects plot for tensile modulus of UT and VT – Composite

The result can be credited to better stress transfer at interface of matrix and alumina nanofibers, which is further enhanced by surface treatment. The three-roll mill process induces high shearing forces as distance between the rollers is decreased, which possibly dealt with efficient de-bundling of alumina nanofibers during each pass. However, it was observed from TEM images at higher loading levels, alumina nanofibers tend to agglomerate which is possibly due to high surface areas of nanofibers, meaning that even though aspect ratio is maintained, they tend to act as stress concentrators, which generally reduces properties. Though surface treatment enabled enhanced properties at all loading levels chosen, when compared to control specimens, suitable loading level at

which properties peaked are more important. Keeping in view results from physical properties testing in chapter 2, it could be said that 25VT - Composite could drastically improve tensile properties without any interference with processing.

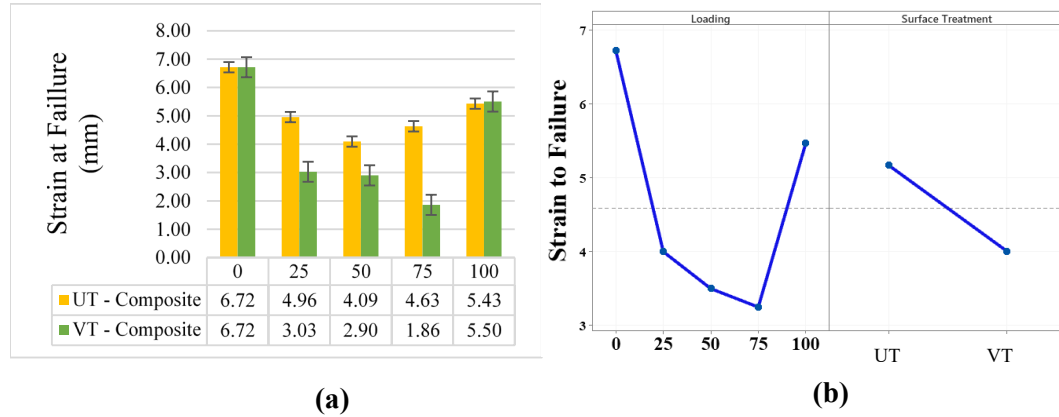


Figure 3.9: (a) Interaction plot and (b) main effects plot of strain at failure UT and VT – Composite

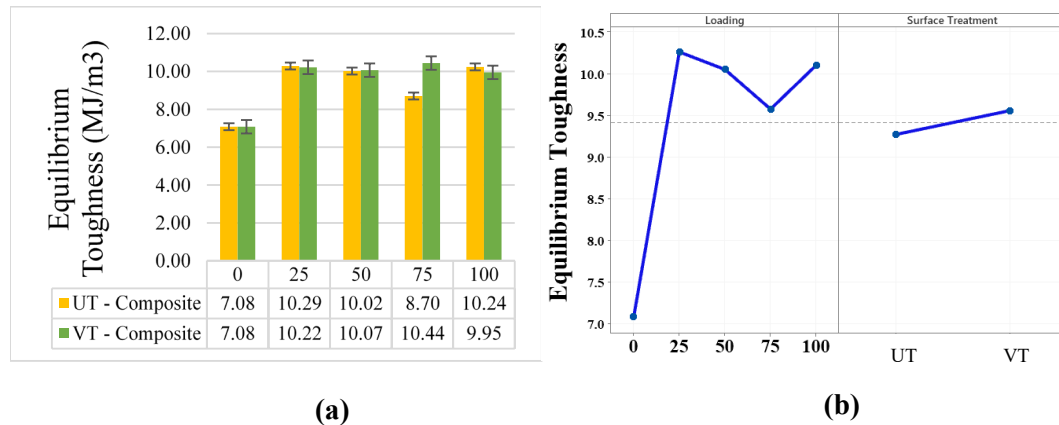


Figure 3.10: (a) Interaction plot and (b) main effects plot for equilibrium toughness of UT and VT – Composite

The strain at failure gives an indication of ductile or brittle property of polymer and it was observed that above 0.75wt% loading level, alumina nanofiber imparted ductility to nanocomposite. The results presented here observed decrease in strain at failure with addition of alumina nanofibers. However, at 1wt% loading level in both untreated and vinyl silane treated alumina nanofibers strain to failure increased. It was observed that surface treatment further reduced strain to failure meaning that composite

behavior is more brittle. Evaporation of vinyl toluene and styrene which are used as reactive diluents in unsaturated polyester resin, is hindered by reactive silane groups on vinyl silane treated alumina nanofibers, because of efficient bonding of chemical groups. Hence due to presence of reactive diluent groups has increased brittleness in composites, which resulted in lower strain to failure. Equilibrium toughness is a measure of ability of a material to absorb energy before failure and is computed by integrating area under curve of tensile stress and tensile strain from zero until maximum stress. It gives an understanding of total strain energy per unit volume induced by applied stress, which is beneficial in designing of composite systems. It was observed that 0.25wt% loading level of alumina nanofibers resulted in increased toughness, which was consistent all through the loading levels selected. Although there is an improvement in energy absorption behavior of material with addition of alumina nanofibers (Figure 3.10), surface treatment had a profound effect on equilibrium toughness as observed. Efficient bonding of alumina nanofibers through vinyl silane surface treatment to matrix resin, provided efficient stress transfer from resin to alumina nanofiber, requiring more energy absorption before failure.

3.4.1.2 Flexure property

The flexure properties as shown in Figure 3.11, shows effect of toughened polyester resin reinforced with glass fiber. Due to unique fiber like morphology, the alumina nanofibers could deflect force, thus causing an increase in properties. However, alumina nanofiber addition had mixed results. At 0.25wt% loading level, flexure strength improved, while further increased loading levels seen a reduction in flexure strength as seen in main plot and interaction plot. However, an initial increase in flexure strength was

observed for 0.25wt%, whereas further increase to 0.5wt% did not yield any improvement. Further loading levels of 0.75wt% and 1wt% has seen a rise in flexure strength. The surface treatment of alumina nanofibers has proven to be effective in increasing in flexural strength and flexural modulus of composites. It is well known that increase in flexure strength and flexure modulus would result in higher toughness values, which is a result of difficulty of crack initiation and propagation within matrix. The interaction plot of two variables loading level and surface treatment reveals that surface treatment improves flexure property due to more surface area available to absorb energy and efficient crack deflection/crack pinning mechanisms. 25VT – Composite showed 12.41% whereas to attain the same improvement, UT-ANF needed a loading of up to 1wt%. In view of increased viscosity at higher loading levels without any surface treatment as shown in figure resulting in processing difficulties and composite fabrication of chapter 2, it is worth mentioning that more prominent results can be attained at lower loadings with surface treatment.

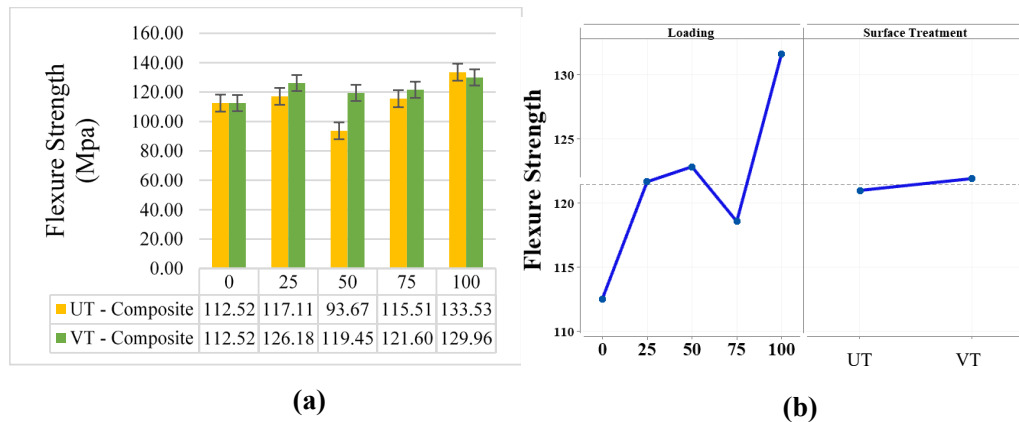


Figure 3.11: (a) Interaction plot and (b) main effects plot for flexure strength of UT and VT - Composite

The main effects plot and interaction plot for flexure modulus as a function of loading level and surface treatment are presented in Figure 3.12. Just as flexure strength

values observed, flexure modulus peaked for 100UT and 100VT - Composite. However, for 25VT - Composite maximum peak values were observed, indicating role of surface treatment on efficient stress transfer leading to improved property when compared to all other loading levels. The flexure modulus dropped for both 50UT and 50VT - Composite. The effect of surface treatment is quite evident from results obtained as improvement in values at any loading level is observed.

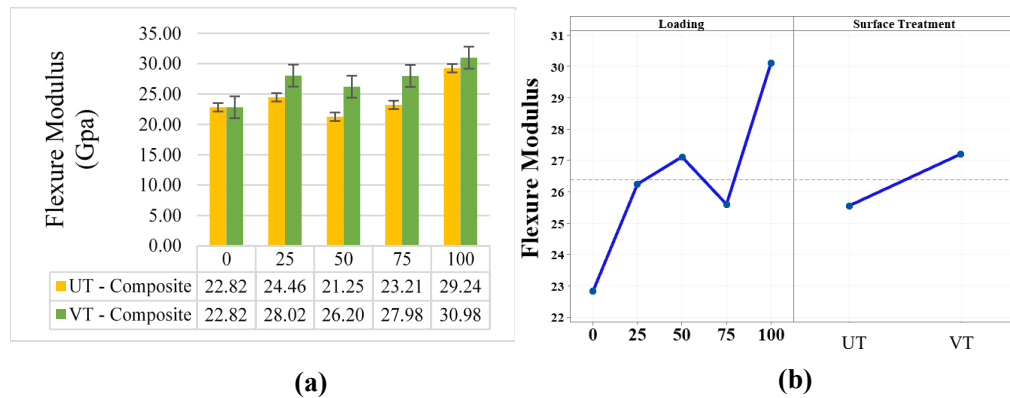


Figure 3.12: (a) Interaction plot and (b) main effects plot for flexure modulus of UT and VT – Composite.

3.4.1.3 Short beam shear property

Interfacial separation between layers or delamination is one of the most common damage mechanisms in laminated composites. Fatigue induced delamination is important in aerospace industry where composites are extensively used. Impact induced delamination aids in energy absorption through progressive failure of composite laminate. Use of nanofillers is prominent method for enhancing interlaminar strength, thus by delaying or suppressing matrix cracking, which eventually leads to delamination. The interlaminar shear property determination also enables the designers to predict residual strength of laminate. In general, the failure modes in interlaminar shear can be either delamination, compression failure on upper face or tension failure on lower face. In some composite laminates, failure mode can also result in inelastic deformation. The

interlocking capability and stress transfer capability of alumina nanofibers in interfacial region of fiber and matrix results in higher short beam property. The short beam strength improved only at 0.25wt% loading level and is more pronounced with surface treatment. Short beam strength is expected to increase because of improvement in matrix strength and fiber matrix interface by filler dispersion, whereas results depicted here is quite composite. Since, void formation, residual stresses, stress concentrations, agglomeration and many other factors play a crucial role in mechanical properties, it is safe to say that since lower void contents are recorded according to the matrix burn-off test 25VT - Composite recorded peak short beam strength values.

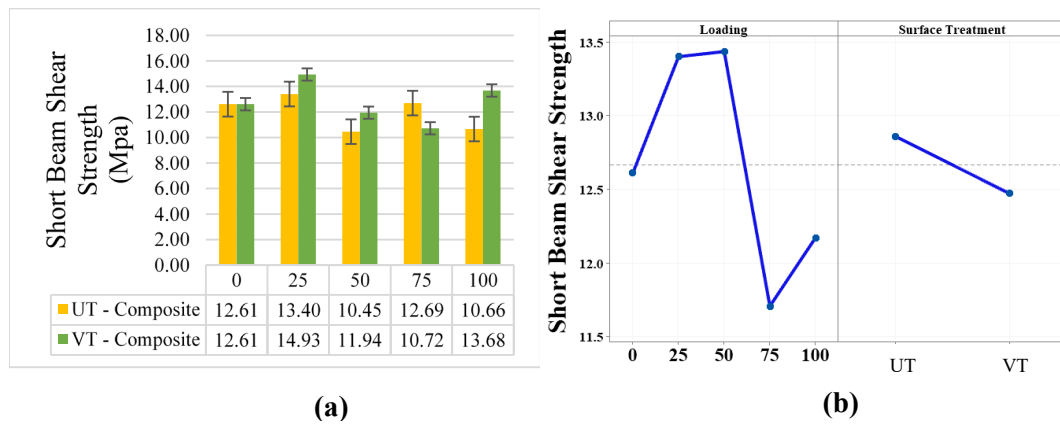


Figure 3.13: (a) Interaction plot and (b) main effects plot for short beam shear strength of UT and VT - Composite

Additional analysis was performed to see the effect of alumina nanofibers and surface treatment on stiffness change of composite as observed from stress strain curves in Figure 3.14 and 3.15. The positive effect of alumina nanofibers was evident from stress-strain plots with improved strength and stiffness in composites. Due to the addition of alumina nanofibers, the curve shifted towards higher strengths and lower strain values, increasing the slope of curve. The slope of tensile stress-strain curve determines modulus of elasticity, which in turn relates to stiffness of composite. Even though stiffness

increased with addition of nanofillers, the 100UT - Composite had observed higher stiffness values as depicted in Figure 3.14. With addition of surface treatment to alumina nanofibers, stiffness values are observed at lower loadings of 0.25wt% and 0.5wt%, proving effectiveness of surface treatment on efficient toughening of matrix and load transfer.

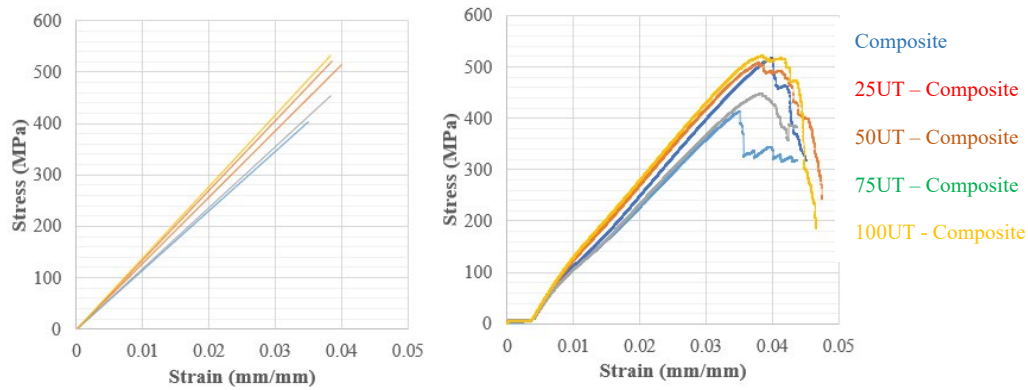


Figure 3.14: Tensile stress-strain plot of UT – Composite

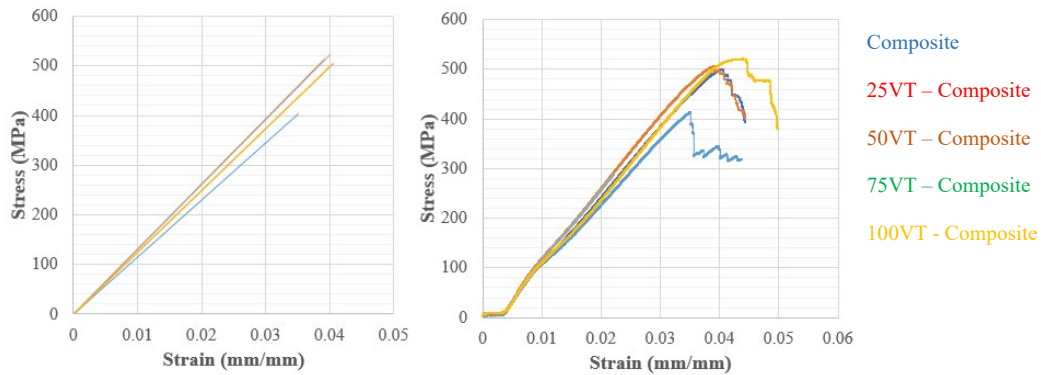


Figure 3.15: Tensile stress-strain plot of VT – Composite

3.4.2. Fracture analysis

Figure 3.16 - 3.24 shows cross-sectional SEM images of samples after short beam testing to understand the damage induced. Control composite and alumina nanofiber modified composites both showed a combination of a variety of damage mechanisms such as matrix cracks, leading to fiber matrix debonding, leading to delamination and fiber pullout. The damage mechanisms are quite expected as it is a complete failure. But

the major distinction between adding alumina nanofibers and surface treatment effects are how composite responded to loading in terms of damage mechanisms. In general, nanofiller modification of matrix enhance adhesion of matrix to fiber due to surface groups provided by the matrix and surface coupling agents added to nanofillers. Thus, addition of nanofillers have a direct effect on interfacial interaction of fiber and matrix.

The fracture analysis of UT – Composite and SEM images are shown in Figure 3.17-3.20. The main damage mechanism observed was cleavages formed through fiber pull out, due to loading level. Fiber pull out is due to weak interfacial interaction between matrix and fiber. Alumina nanofibers, since they do not have any surface treatment, showed weaker interaction. However, matrix toughening mechanism due to addition of alumina nanofibers is observed in which the crack propagation is restricted and deflected. The crack deflection due to nanofiller lead to extensive fiber-matrix debonding which caused fiber pullout. The fiber-matrix debonding eventually lead to delamination between different fiber roving's and eventually between layers. The fiber breakage is visible at all loading levels of alumina nanofibers. A closer look at fibers revealed that surface is clearer, without any matrix adhesion on to fibers. Hence even though there is no evident interaction of interfaces of matrix and fiber, increase in short beam strength is due to efficient deflection of matrix cracks generated. In contrast to damage mechanisms observed for 25UT, 50UT and 75UT – Composite, 100UT - Composite observed less fiber matrix debonding and delamination. In addition to that matrix rich regions along with fiber enveloped with matrix is observed meaning interfacial strength increased at 1wt% loading level. Irregular matrix cracking along with irregular fiber breakage was observed with limited signs of fiber pullout. Alumina nanofiber loading level above

0.75wt% has a greater effect on interaction of matrix with fiber, which lead to increase in short beam strength property at 1wt%.

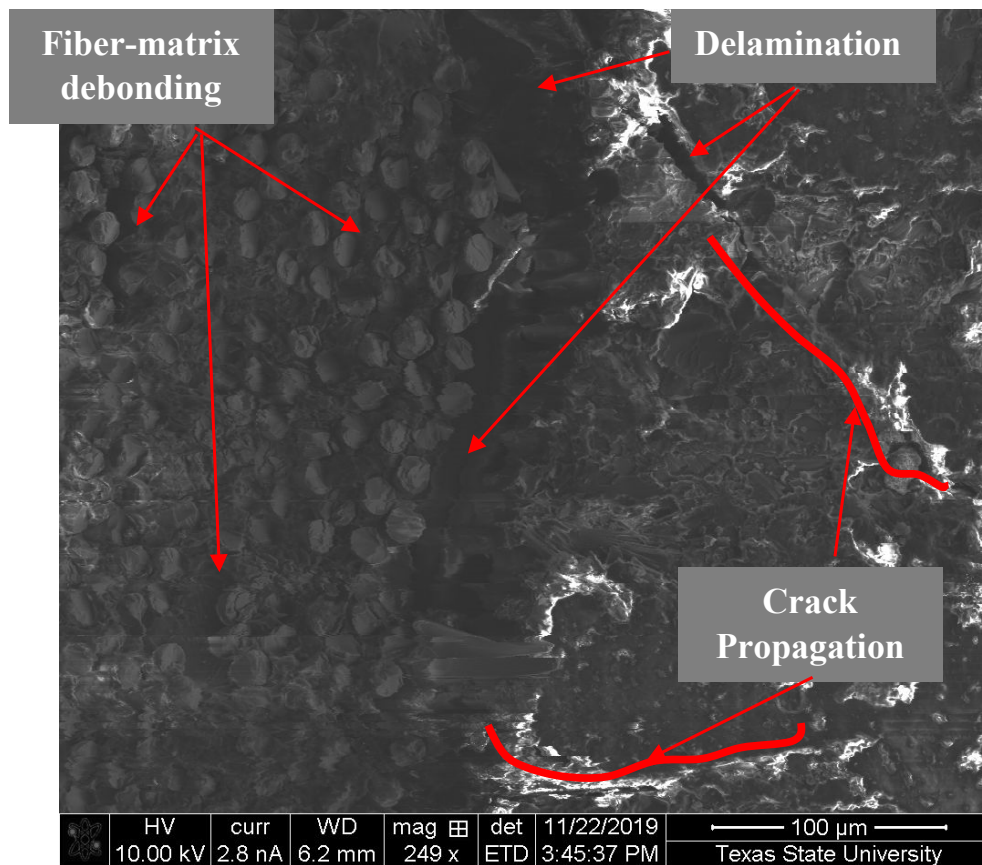


Figure 3.16: SEM imaging of Composite.

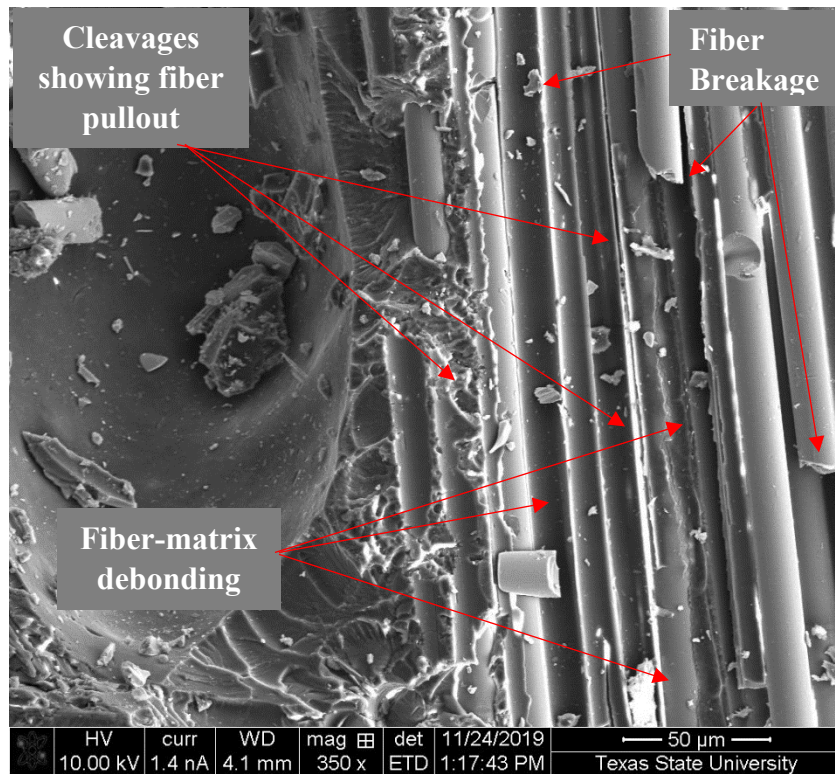


Figure 3.17: SEM imaging of 25UT – Composite.

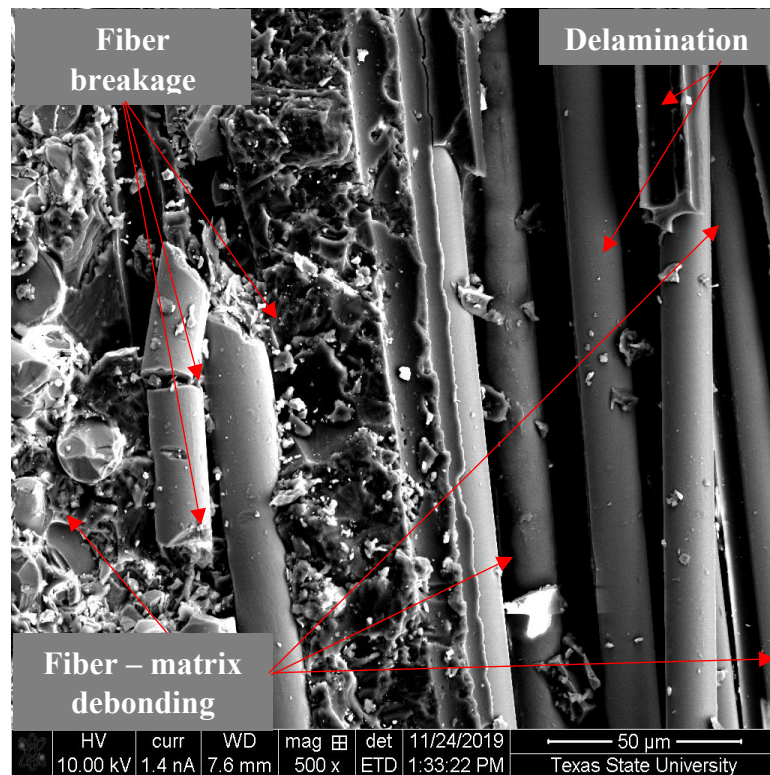


Figure 3.18: SEM imaging of 50UT – Composite.

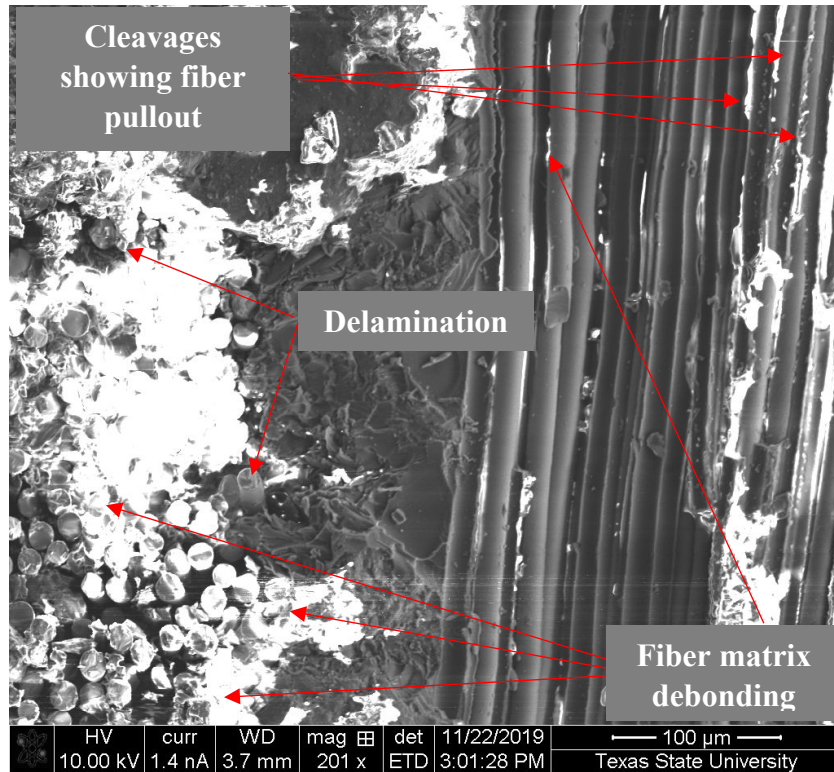


Figure 3.19: SEM imaging of 75UT – Composite.

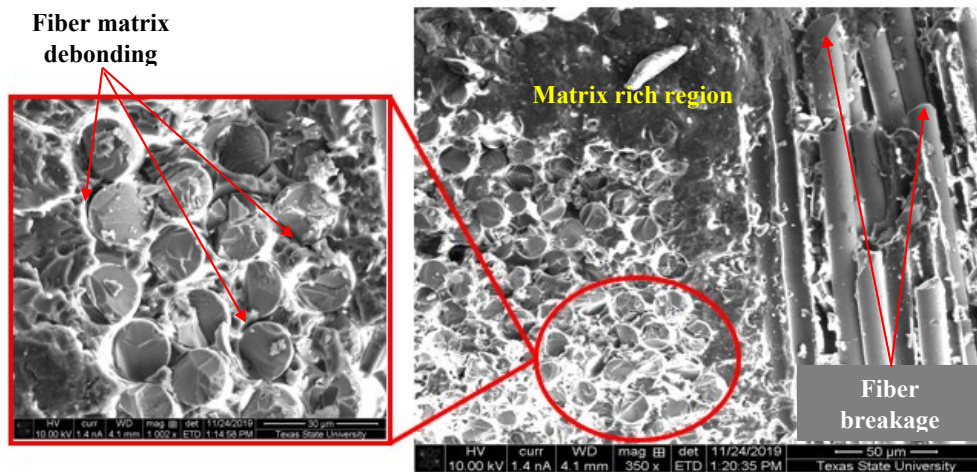


Figure 3.20: SEM imaging of 100UT – Composite.

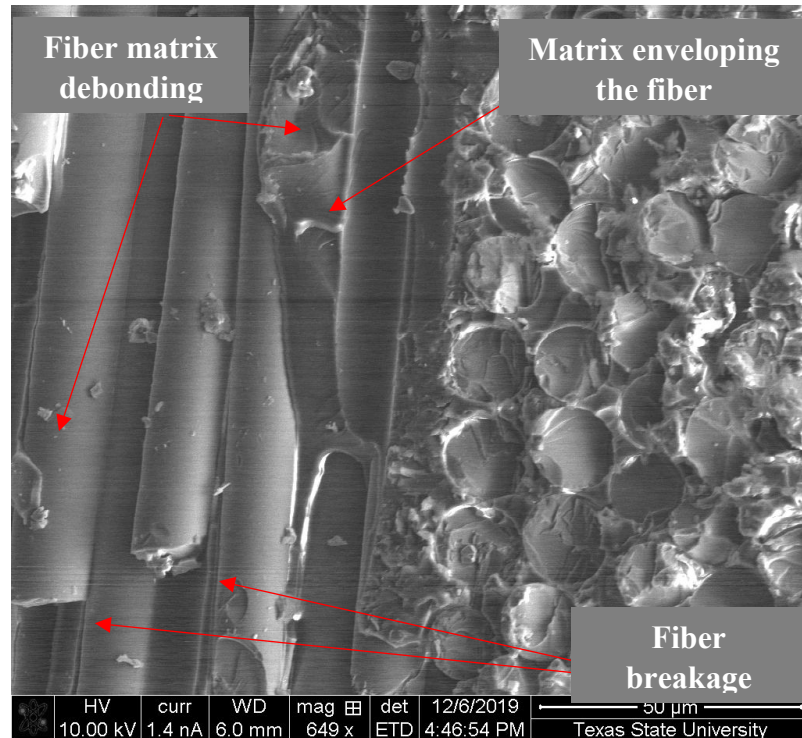


Figure 3.21: SEM imaging of 25VT – Composite.

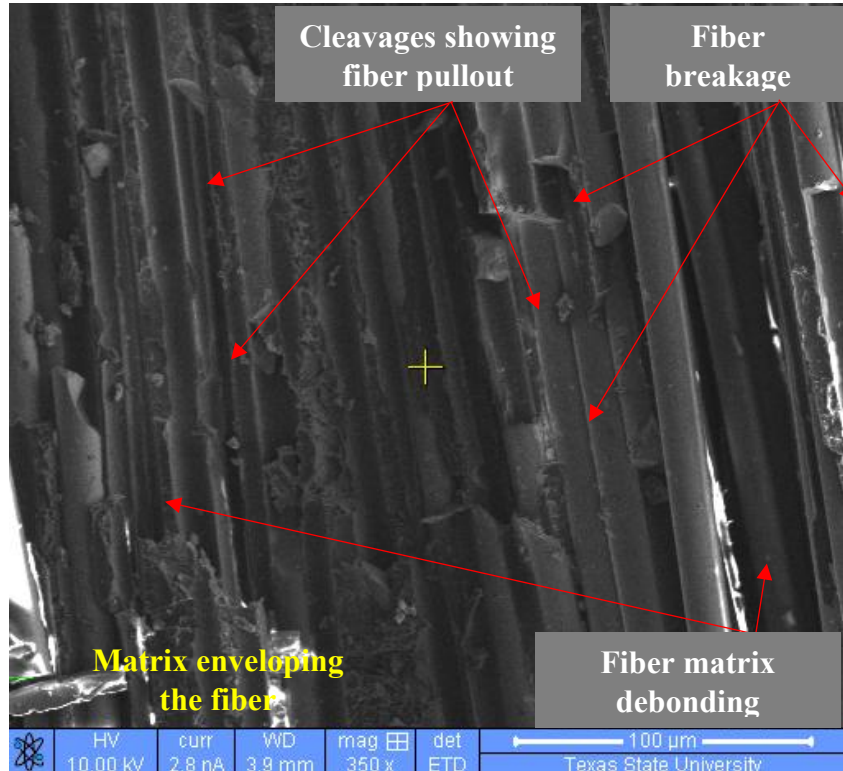


Figure 3.22: SEM imaging of 50VT – Composite.

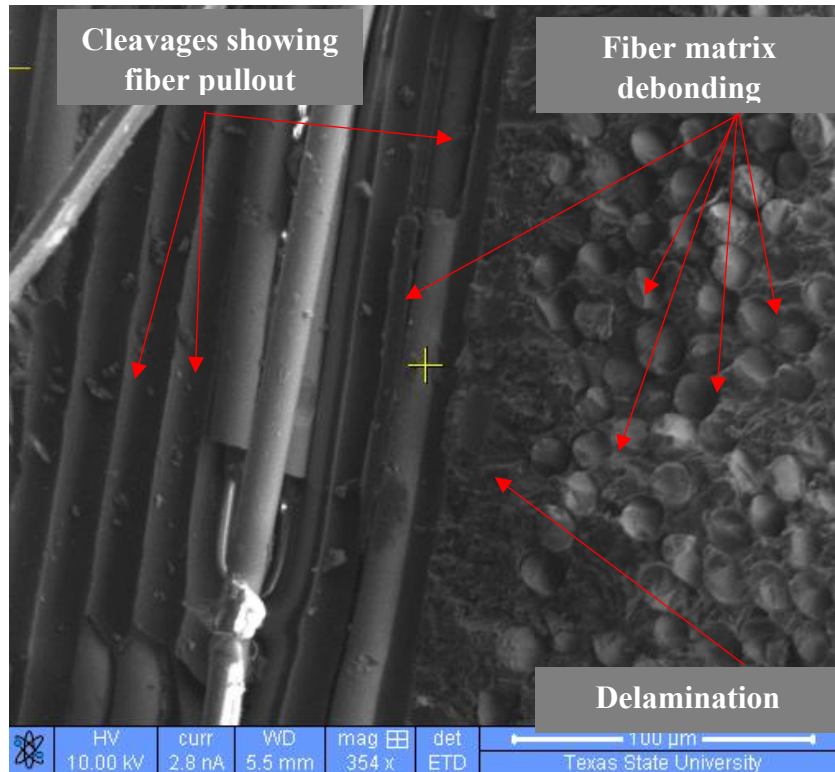


Figure 3.23: SEM imaging of 75VT – Composite.

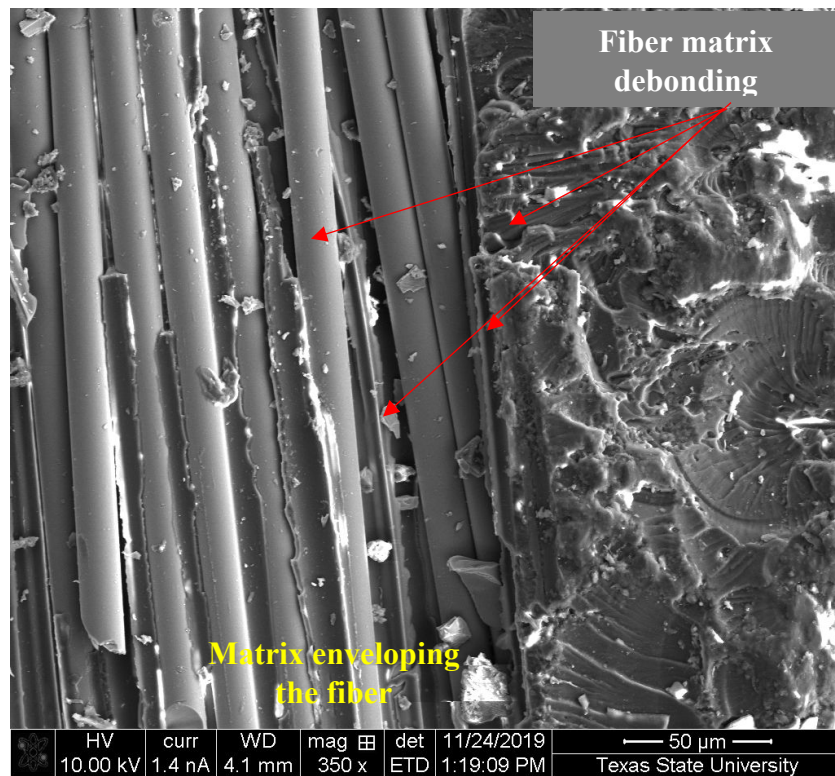


Figure 3.24: SEM imaging of 100VT – Composite.

The VT - Composite fracture analysis images are shown in Figure 3.21 - 3.24.

The effect of surface treatment of alumina nanofibers is evident from fracture analysis as matrix enveloped the fibers restricting fiber pull out. For 25VT - Composite as shown in Figure 3.21, showed very limited signs of fiber matrix debonding and delamination, but fiber breakage was observed. It is evident from this analysis that silane coupling agent promoted adhesion between alumina nanofibers, matrix, and fiber. The efficient stress transfer between efficiently bonded constituents resulted in higher interlaminar strengths manifested according to interaction plots and percentage improvement. For VT - Composite damage is more pronounced showing neither the effect of alumina nanofiber nor the effect of surface treatment. More pronounced fiber matrix debonding, delamination, fiber breakage and extensive damage was observed. Surface treatment resulted in efficient bonding of nanofiller and matrix because of rough surfaces as observed in the image. There are matrix rich regions which efficiently transferred stress from matrix to fiber. However, the effect was not obvious, as nanofillers were not effective in crack deflection to interface region. For 75VT - Composite, effect of surface treatment is observed, because of the presence of rough surface on fiber, indicating adherence of matrix on fiber surface. 0.25wt% loading level, less fiber matrix debonding is observed, however due to excessive debonding between individual roving's lead to eventual delamination in laminate resulting in less short beam strength as compared. At 1wt% loading level, short beam strength regained due to fiber enveloped by matrix resisting fiber pullout causing efficient stress transfer. Although there is fiber damage and fiber matrix debonding to some extent, silane coupling agent effect on maintaining interfacial strength helped in increase of property. The matrix rich region observed

encapsulating fibers show matrix crack propagation and energy absorption by deflecting matrix cracks.

When compared between UT - Composite and VT - Composite, it was observed that polyester adheres to fiber surface, indicating improvement in interfacial adhesion, which is stronger than matrix strength itself. Significant plastic deformation resulted in enhanced mechanical properties of VT - Composite due to matrix enveloped fibers. The rough surfaces as observed in VT -Composite acts as interlocking increasing energy to failure and suggests enhanced interface and higher friction coefficient which is promoted by silane coupling agent on surface of alumina nanofibers. Hence damage mechanism in VT - Composite changed from fiber matrix debonding to fiber matrix debonding along with resin breakage. While failure at interface is predominant in UT - Composite, matrix breakage is more predominant in VT - Composite.

3.5 Statistical analysis

There was a wide variation of test results obtained from nanofiller modification of polyester resin. To determine statistical significance of data we ran Analysis of Variance (ANOVA) using Minitab software to analyze changes in properties. ANOVA was used keeping confidence interval of 95%, indicating significant level of 0.05, to study significance of regression model and effect of each factor, interaction effects on measured response and to find significant factors. The computed statistical results (probability values) are compared to a significant level of confidence 0.05 to determine whether observed data for factors considered were significant. In general, if probability value is less than or equal to 0.05, null hypothesis is rejected, and alternate hypothesis is confirmed. Statistical analysis carried out include determination of each independent

variable (alumina nanofiber) and two-way interactions (alumina nanofiber and surface treatment). The general regression linear model used for experimental design was:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \dots + \varepsilon \quad (1)$$

where y is the response, X_1 and X_2 are variables, β_0 is constant term, β_1 and β_2 are coefficients of polynomial for linear effects, β_{12} is the coefficient of polynomial for interaction effect and ε is the error. The response variables are limited to mechanical properties namely tensile strength, tensile modulus, equilibrium toughness, strain to failure, flexure strength, flexural modulus, and short beam strength in this study. The regression analysis presented here is the outcome of factors (Alumina nanofibers, surface treatment) and their interactions (alumina nanofibers and surface treatment) on above considered responses. Table 3.5 presents general linear model with statistical significance for selected responses in combination with predictors. Generally, positive sign in the models has a positive effect on responses while a negative sign has a reducing effect. Table 3.6, 3.7 and 3.8 show coefficients of respective factors and P- values representing statistical significance of properties. The R^2 value shown in ANOVA represents proportion of variance in response data explained by terms in the model. The difference between R^2 and R^2 (adj.) values implies non-significant terms consisted in the model. The less difference between the R^2 and R^2 (adj.) indicates model was statistically significant and reliable to predict properties within range of studies. Similarly, R^2 (pred.) values also give information about predictive ability of the model generated using regression analysis. All the mechanical properties showed less values for R^2 , R^2 (adj.) and R^2 (pred.) values meaning that models generated has less predictive ability on response as a function of predictors. However, the models generated for physical properties as a

function of predictive variables showed that the model generated has greater predictability.

Table 3.5: General linear regression model for each response

Response	Linear Models
Tensile Strength	$y = 452.2 + 60.4 (\text{wt}\%) - 5.2 (\text{ST}) + 32.4 (\text{wt}\% \times \text{ST})$
Tensile Modulus	$y = 17.96 + 4.30 (\text{wt}\%) + 2.37 (\text{ST}) + 0.93 (\text{wt}\% \times \text{ST})$
Equilibrium Toughness	$y = 4.38 + 5.66 (\text{wt}\%) + 3.98 (\text{ST}) - 3.28 (\text{wt}\% \times \text{ST})$
Strain at failure	$y = 5.73 - 1.11 (\text{wt}\%) - 1.01 (\text{ST}) - 0.34 (\text{wt}\% \times \text{ST})$
Flexure Strength	$y = 107.15 + 13.1 (\text{wt}\%) + 8.8 (\text{ST}) - 1.2 (\text{wt}\% \times \text{ST})$
Flexure Modulus	$y = 21.53 + 6.03 (\text{wt}\%) + 2.41 (\text{ST}) + 0.48 (\text{wt}\% \times \text{ST})$
Short Beam Strength	$y = 12.28 + 0.57 (\text{wt}\%) + 0.91 (\text{ST}) - 1.40 (\text{wt}\% \times \text{ST})$

Table 3.6: Summary of analysis of variance for tensile properties

Term	Tensile Strength		Tensile Modulus		Equil. Toughness		Strain at Failure	
	Coef	P-Value	Coef	P-Value	Coef	P-Value	Coef	P-Value
Constant	452.2	0.000	17.96	0.000	4.38	0.097	5.73	0.005
Wt%	60.4	0.298	4.30	0.196	5.66	0.171	-1.11	0.634
ST	-5.2	0.914	2.37	0.391	3.98	0.254	-1.01	0.617
Wt% x ST	32.4	0.680	0.93	0.832	-3.28	0.548	-0.34	0.918
R ²	43.10		59.75		42.87		23.22	
R ² (adj.)	14.66		39.63		14.30		0.00	
R ² (pred.)	0.00		0.00		0.00		0.00	

Table 3.7: Summary of analysis of variance for flexure and short beam property.

Term	Flexure Strength		Flexure Modulus		Short beam strength	
	Coef	P-Value	Coef	P-Value	Coef	P-Value
Constant	107.15	0.000	21.53	0.000	12.28	0.000
Wt%	13.1	0.358	6.03	0.127	0.57	0.792
ST	8.8	0.470	2.41	0.445	0.91	0.631
Wt% x ST	-1.2	0.951	0.48	0.923	-1.40	0.651
R ²	35.84		60.54		4.38	
R ² (adj.)	3.76		40.81		0.00	
R ² (pred.)	0.00		0.00		0.00	

The normal probability plots give information about the reliability of ANOVA results. If the data points fall near straight line, it is safe to say that data is reliable. The

residuals as indicated in Figure 3.25 for all mechanical responses are close to straight line indicating normal distribution of data points.

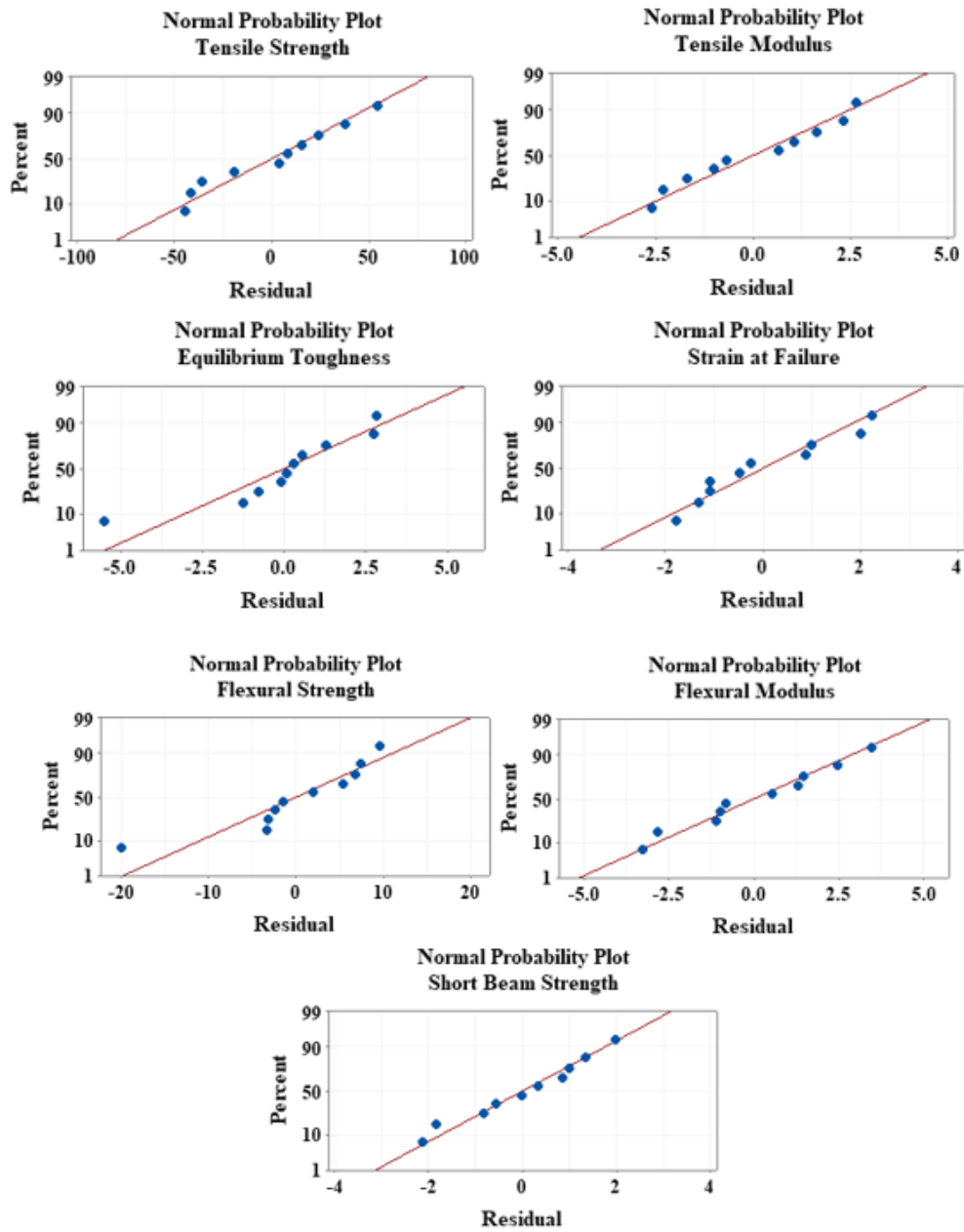


Figure 3.25: Normal probability plots of mechanical responses.

3.6 Conclusions

1. Void fraction analysis was carried out to assess the quality of composite in terms of fiber volume fraction and void volume fraction. It was observed that with increase of alumina nanofiber content, void volume fraction increased. With addition of surface treatment however, void content has decreased. It was worth mentioning that the viscosity increases with addition of alumina nanofibers cause increase in void content.
2. The layup and compression molding procedure resulted in high fiber content because of squeezing of excess resin content during wetting of fabric using resin drip bath and processing.
3. The tensile strength of composites increased with addition of alumina nanofibers and it was observed that surface treatment had no significant effect on tensile strength. It was observed that 25UT – Composite, 100UT – Composite and 100VT -Composite had approximately the same improvement of approximately 27% in tensile strength.
4. A major factor distinguishing improvement in composites and modification of nanofillers with silane coupling agent is tensile modulus values. Since modulus determines stiffness of composite, it was observed that surface treatment of alumina nanofibers enhanced stiffness of the composites by three folds.
5. The increase in flexure strength was maximum for VT - Composite composites. For 0.25wt%, 0.5wt%, 0.75wt% and 1wt% improvement in flexure property was 12.14%, 6.16%, 8.07% and 15.2% respectively.
6. Flexure modulus values peaked for VT - Composite by a value of 22.79%, 14.81%, 22.61% and 35.57% at loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt%

- respectively. Efficient stress transfer between surface treated alumina nanofiber, polyester matrix and glass fiber manifested higher peak loads.
7. The short beam strength peaked for 25VT - Composite with a maximum improvement of 18.40%. Short beam strength failure of composites is important out-of-plane property which is useful in evaluating maximum improvement in impact related property.
 8. The fracture analysis using SEM imaging, revealed that interfacial strength is increased with addition of surface treatment to alumina nanofibers. The damage mechanisms revealed that for UT - Composite extent of fiber-matrix debonding, delamination, fiber breakage and fiber pullout were extensive. However, VT - Composite showed limited signs of fiber matrix debonding, delamination because of interaction between nanofiller, matrix and fiber showing effectiveness of surface treatment. The roughness of fiber surface noted adherence of matrix to glass fiber surface indicating improvement in interfacial adhesion. The damage mechanism changed from fiber matrix debonding to matrix breakage indicating improved interfacial strengths stronger than matrix strength itself.
 9. Considering the effects of viscosity increase which limits processability, void fraction content which inhibits quality of laminate and interferes with mechanical properties, the mechanical property studies, percentage improvements and fracture analysis, it can be said that 0.25wt% loading level of alumina nanofiber with surface treatment is optimal for significant increase in property.
 10. For each response, a model is provided with their adequacy investigated, based on experimental data. - The linear regression model did not show good fit or good

accuracy based on the R^2 , R^2 (adj.) and R^2 (pred.) values, Choosing the best nonlinear functions that expect or describes the relationship of response and predictors is imperative to assess significance of test data.

11. It is imperative to consider using different silane coupling agents compatible with polyester and alumina nanofibers to evaluate their effects on mechanical properties at reduced viscosity and homogenous dispersion.

4. ALUMINA NANOFIBER FILLED POLYESTER NANOCOMPOSITES: THERMAL CHARACTERIZATION

Thermal characterization of polymeric materials includes study of material physical property changes under influence of thermal variations (heat or cool). Addition of nanofillers to thermoset resins such as unsaturated polyester resin can alter thermal stability of resin and modify mechanical/chemical bonding with reinforcement. In fact, nanofiller addition inhibits curing reaction, representing additional efforts and process optimization for commercial production. Unsaturated polyester resin has gained prominence in automotive and commodity composite industries. Industrial unsaturated polyesters are typically processed using organic diacids and glycols. Often reactive diluents such as styrene or toluene are used as cross-linking monomers which also prevent chemical reaction before processing. Unsaturated polyester cures by free radical polymerization and the curing mechanism is given in Figure 4.1.

During chemical cross linking of unsaturated polyester resins, the presence of reactive styrene monomer and other solvents pose a challenge by micro-gelation causing curing problems. The unsaturated polyester resin cure reaction involves complex mechanisms such as initiation, propagation, and termination. In the initiation stage, initiator decomposes chemically giving free radicals and in later stage these radical react with monomers thus promoting curing process. Once the double bonds are completely saturated crosslinking terminates. Styrene is a volatile reactive component which is used to maintain viscosity of unsaturated polyester resin and significant loss of styrene can alter cure kinetics/processing of composite material systems.

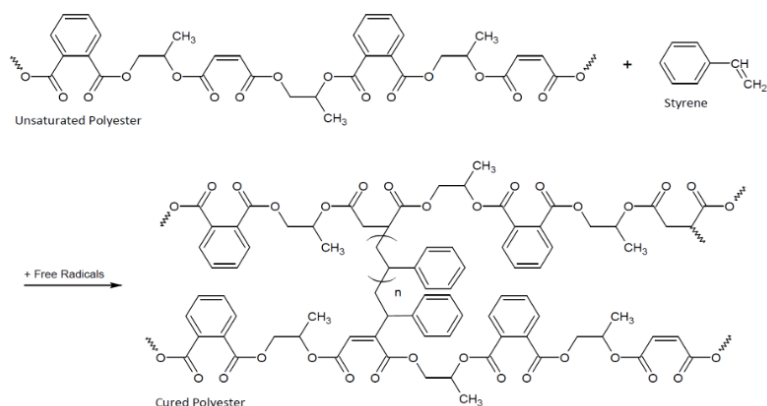


Figure 4.1: Free radical curing mechanism of UPE.

Researchers have used a variety of thermal analysis techniques such as dynamic mechanical analyzer (DMA), thermo mechanical analyzer (TMA), differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) to determine kinetics of unsaturated polyester resin under isothermal and dynamic conditions. The present study utilizes data collected from thermogravimetric analysis and dynamic scanning calorimetry to determine effect of alumina nanofibers on thermal characteristics such as mass loss, degree of curing and glass transition temperature. Since present research uses surface modification of alumina nanofibers using vinyl silane coupling agent, analysis is performed to determine influence of surface treatment on stabilization of alumina nanofiber in the polyester resin. The discovery SDT 650 used for thermal analysis is shown in Figure 4.2.

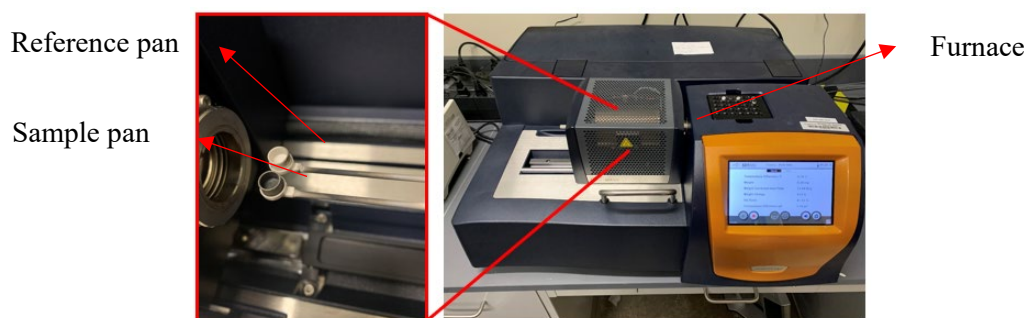


Figure 4.2: Simultaneous DSC and TGA (SDT) equipment.

4.1 Characterization techniques

4.1.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) measures weight change and rate of weight change as a function of time and temperature. The information related to decomposition kinetics, oxidation kinetics, moisture content, reactive or corrosive atmosphere could help researchers in processing polymers and selecting appropriate nanofillers for polymer thermal property enhancement. Thermogravimetric analysis of nine types of material system are performed using Discovery SDT650 simultaneous DSC/TGA system from TA instruments according to ASTM E2550 standard. Heating rate selected was 5C/min, 10C/min and 15C/min from 30C to 650C for resin coupon samples. The sample weight was in between 7mg to 10mg. TGA analysis was performed on untreated alumina nanofiber and vinyl silane treated nanofiber at 10C/min from room temperature to 1000C to quickly determine presence of silane agent.

4.1.2 Activation energy

The minimum energy required to start a chemical reaction is defined as activation energy and can be measured using various isoconversion methods. Activation energy calculation enables researchers to understand the effects of individual components on thermal behavior of unsaturated polyester resin under influence of nanofillers and any surface treatments. Readers are suggested to refer to Starink M.J. article on determination of activation energy from linear heating rate experiments (Starink, 1997) to gain an understanding on different methods to calculate activation energy and their accuracy. The rate of decomposition process is a relation of temperature (T) and conversion rate (α). The conversion rate at a given temperature is determined using equation 1

$$\alpha = \frac{w_o - w_T}{w_o - w_f} \quad 1$$

where w_o , w_f and w_T are initial mass, final mass and mass at temperature T .

The conversion rate α is calculated as a product of function of temperature $k(T)$ and function of conversion $f(\alpha)$. The basic rate equation used for kinetic studies is given in equation 2.

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad 2$$

The temperature dependent function is given by Arrhenius equation

$$k(T) = A \exp(-E_a/RT) \quad 3$$

where A is the pre-exponential factor, E_a is the activation energy and R is the universal gas constant (8.314).

The Flynn-Wall-Ozawa (FWO) (Flynn, 1983) approximation for estimating activation energies is given by equation

$$\ln \beta = \ln (AE_a(\alpha)/R) - 5.33 - \ln(1-\alpha) - 1.05 (E_a/RT(\alpha)) \quad 4$$

The slope of plot of $\ln \beta$ against $1/T$ gives activation energy E_a .

The activation energies determined by FWO approximation are compared with Lyon's method (Lyon, 1997) in which activation energy is expressed as:

$$E_a(\alpha) = -R \left[\frac{d \ln \beta}{d \left(\frac{1}{T(\alpha)} \right)} + 2T(\alpha) \right] \quad 5$$

The parameters required for activation energy calculations are calculated from TGA analysis and TGA curves at 5C/min, 10C/min and 15C/min heating rate.

4.1.3 Differential scanning calorimetry

The differential scanning calorimetry (DSC) scans were performed using Discovery SDT 650 from TA instruments. The scans were conducted at 10C/min heating rate from room temperature to 650C in nitrogen atmosphere. The mass of samples was maintained in between 7mg and 9mg with empty aluminum crucible as reference pan. Test results were reported according to ASTM E794 standard("Standard Test Method for Melting And Crystallization Temperatures By Thermal Analysis,").

4.2 Results and discussion

4.2.1 Thermogravimetric analysis

The TGA analysis plots of untreated alumina nanofiber and vinyl silane treated alumina nanofiber is presented in Figure 4.3 and Figure 4.4. TGA analysis was performed to verify presence of silane coupling agents on alumina nanofibers at 10°C/min ramp rate up to 1000°C in nitrogen atmosphere. The first derivative of TGA (DTGA) curve is plotted to detect minute changes in mass loss. From TGA curves, presence of silane coupling agent can be verified due to change in slope of mass loss curve in a temperature range between 200°C to 450°C. Most commercially available silane coupling agents have organic functionality separated from silicon atom by carbon atoms. It was noted that vinyl-based silane coupling agents are thermally stability temperature range of 220-360C. The same results were observed in this study. Further TGA analysis was performed on nine material systems are presented in Figure 4.4. It was observed that there is a positive contribution of alumina nanofibers as well as surface treatment on thermal decomposition of nanocomposites. From TGA plots, lower onset degradation temperature at 10wt%

mass loss, temperature at 50wt% mass loss and temperature at peak loss were extracted and presented in Table 4.1.

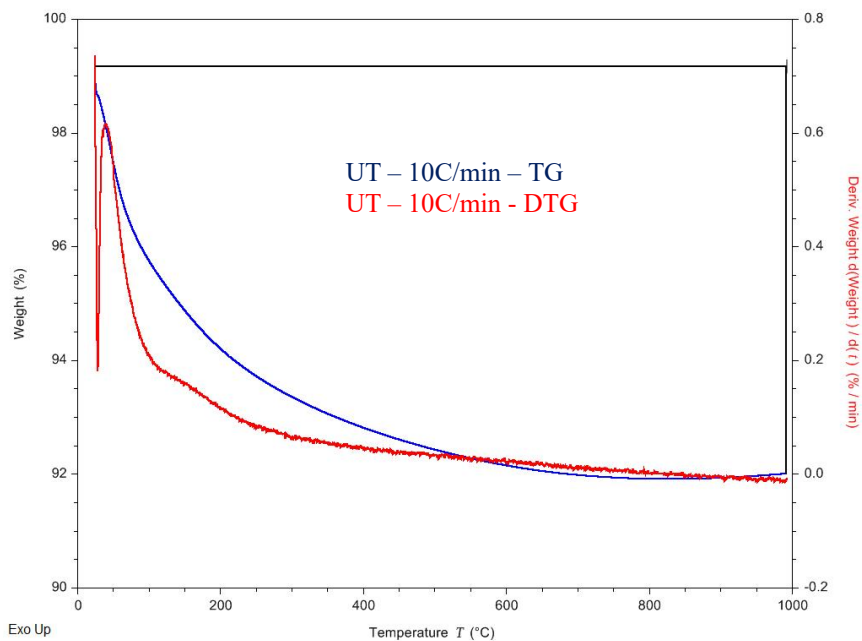


Figure 4.3: TGA and DTGA plot of untreated alumina nanofiber

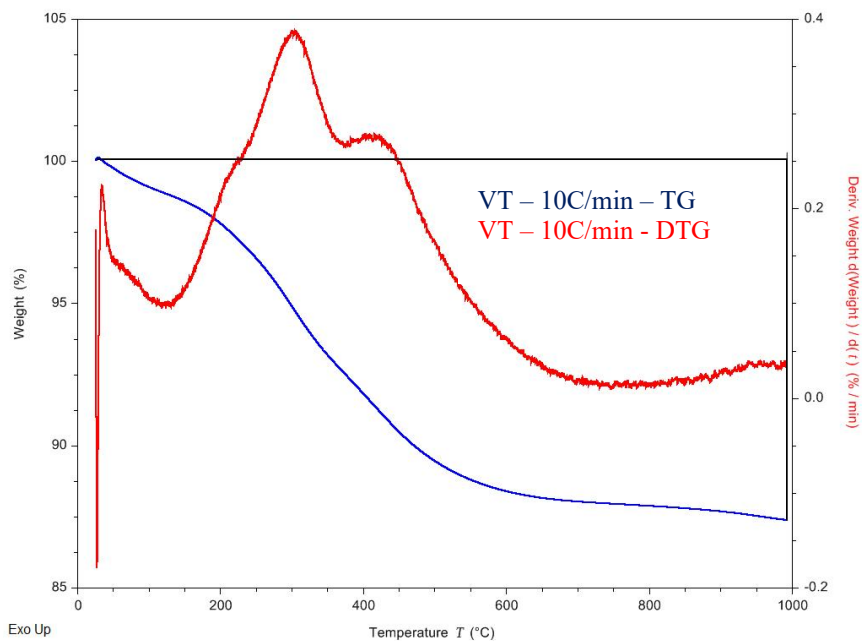


Figure 4.4: TGA and DTGA plot of vinyl silane treated alumina nanofiber

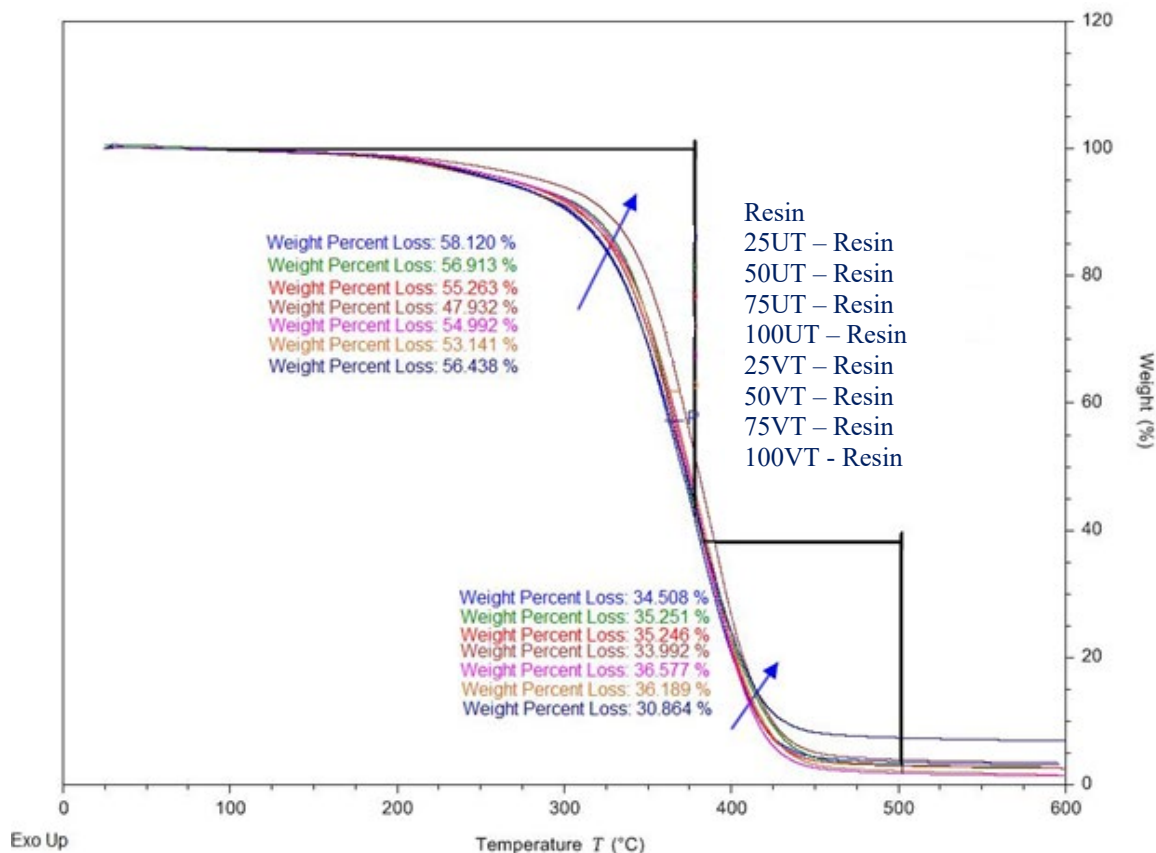


Figure 4.5: Consolidated TGA plots of UT and VT - Resin

Table 4.1: Summary of lower onset decomposition, 50wt% decomposition and peak mass loss temperature from TGA analysis

Sample	T _{dec} (0.1)		T _{dec} 50wt%		Peak mass loss temperature	
	UT - Resin	VT - Resin	UT - Resin	VT - Resin	UT - Resin	VT - Resin
0	305.30		370.24		417.94	
25	309.94	315.22	372.35	371.92	424.37	371.18
50	313.37	327.12	374.09	380.05	422.61	418.33
75	303.32	308.61	372.11	374.76	421.98	418.08
100	307.29	319.20	370.91	376.83	430.31	429.58

It was observed from the data that lower onset degradation temperature enhanced with surface treatment of alumina nanofibers due to promoted bonding which requires higher energies for bond dissociation. The thermal stability of a polymer is often expressed by its T_{dec} (0.5) (decomposition temperature at which 50wt% mass loss is observed) and plots of thermal stability as a function of alumina nanofiber/surface

treatment are presented in Figure 4.5. With increasing loading levels of alumina nanofibers, it was observed that the $T_{dec} (0.5)$ value increased indicating positive effect of nanofillers on thermal stability. However, only a 4°C change is observed at 0.5wt% loading level of untreated alumina nanofiber. Whereas, in case of vinyl silane treated alumina nanofibers, $T_{dec} (0.5)$ increased by 10°C. Enhanced bond interaction between , nanofillers and polymer surface groups increases bond dissociation energy, thus contributing to higher thermal stability (M. K. Hossain, Hossain, Hosur, & Jeelani, 2010; Oza, Ning, Ferguson, & Lu, 2014). Further kinetics and thermal parameters are studied for material systems from data obtained from TGA.

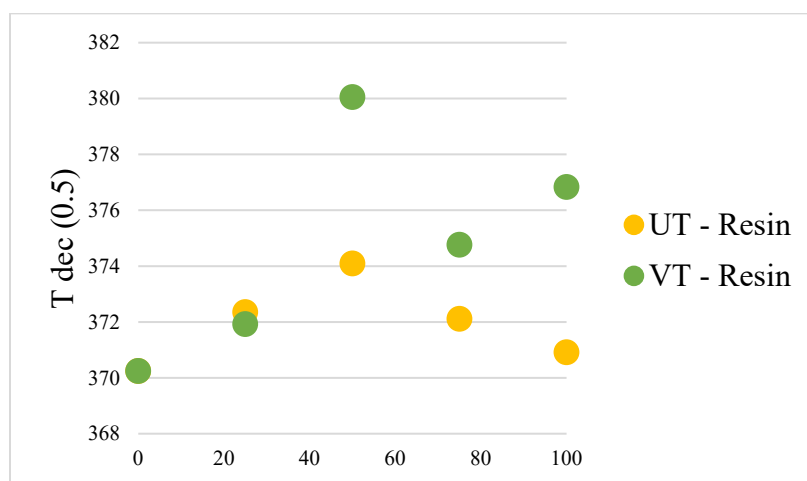


Figure 4.6: Thermal stability of UT and VT – Resin as observed from $T_{dec} (0.5)$

4.2.2 Activation energy

TGA plots for individual material systems under three heating rates 5C/min, 10C/min and 15C/min are presented in Figure 4.6-4.14. It was observed from thermographs that there is a single step decomposition for all samples with consistent shift. The $\ln\beta$ vs $1/T(\alpha)$ plots were also shown in same figure for respective material systems. The activation energies are calculated for each material system by calculating slope of $\ln\beta$ vs $1/T(\alpha)$ plots. The activation energies at different conversion ratios for all

material systems according to FWO method are plotted in Figure 4.15. The averages of activation energies calculated using Lyons method are presented in Figure 4.16 and compared with FWO method of activation energies.

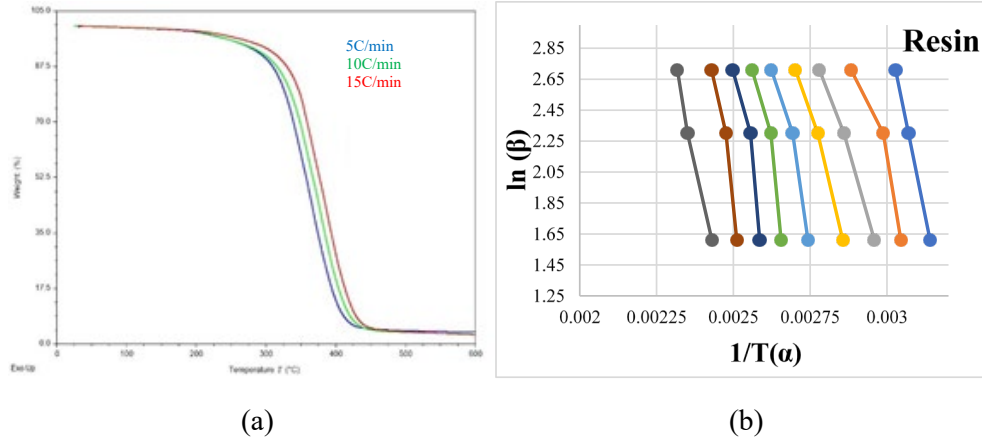


Figure 4.7: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for resin

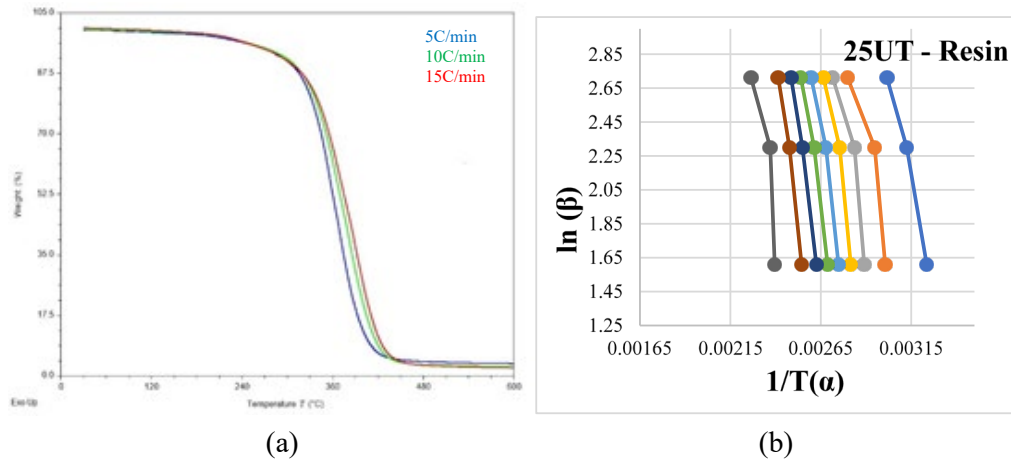


Figure 4.8: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 25UT - Resin

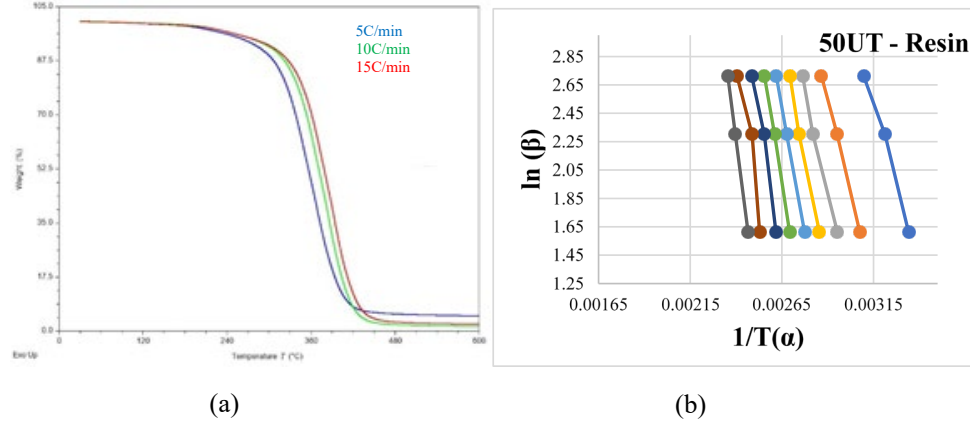


Figure 4.9: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 50UT – Resin

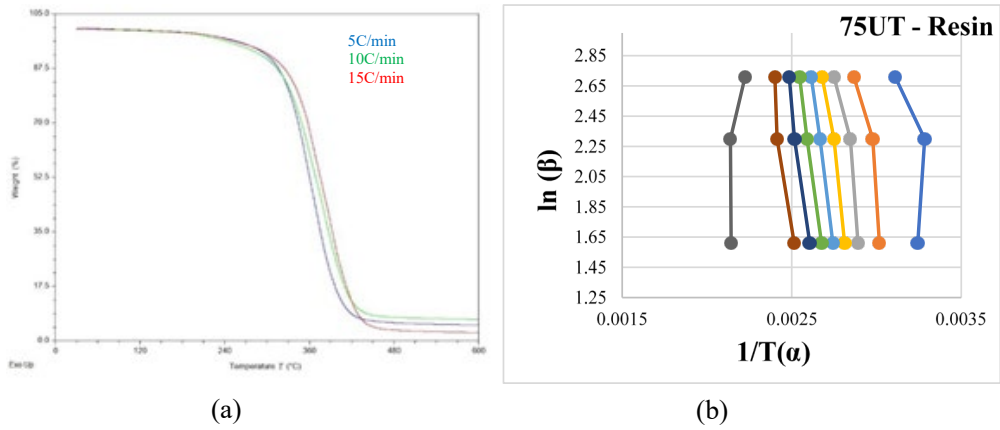


Figure 4.10: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 75UT – Resin

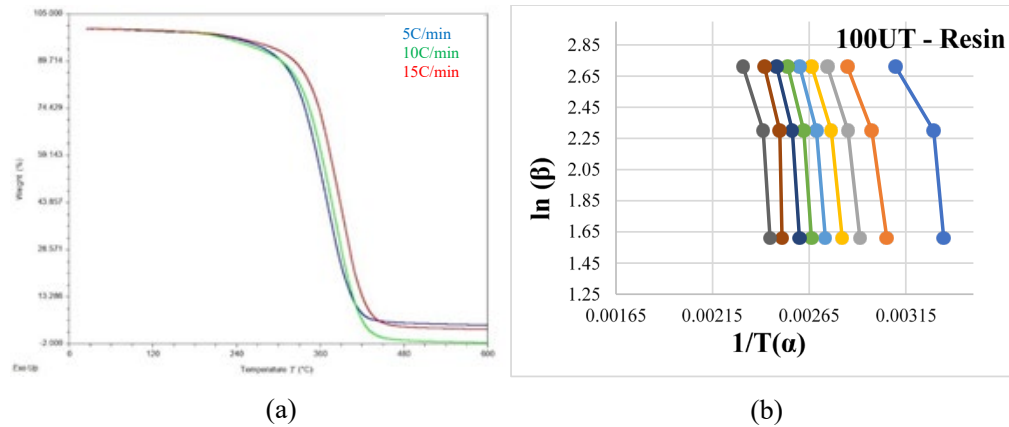


Figure 4.11: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 100UT - Resin

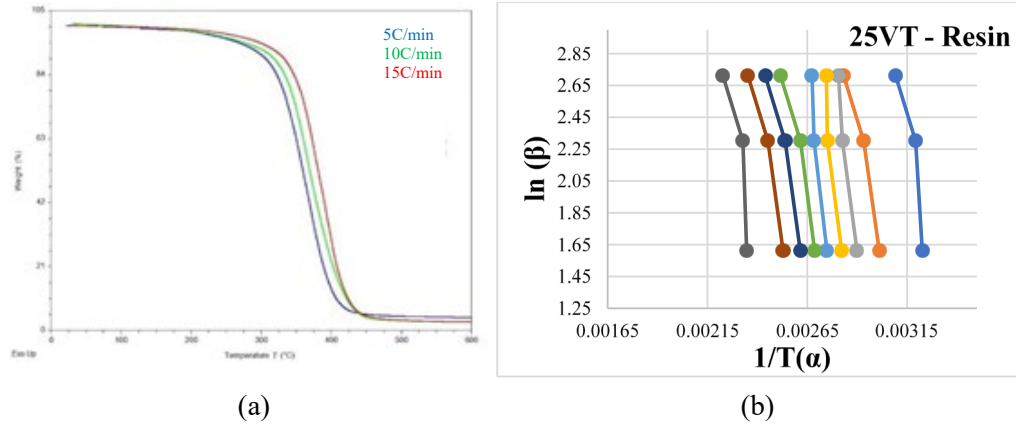


Figure 4.12: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 25VT – Resin

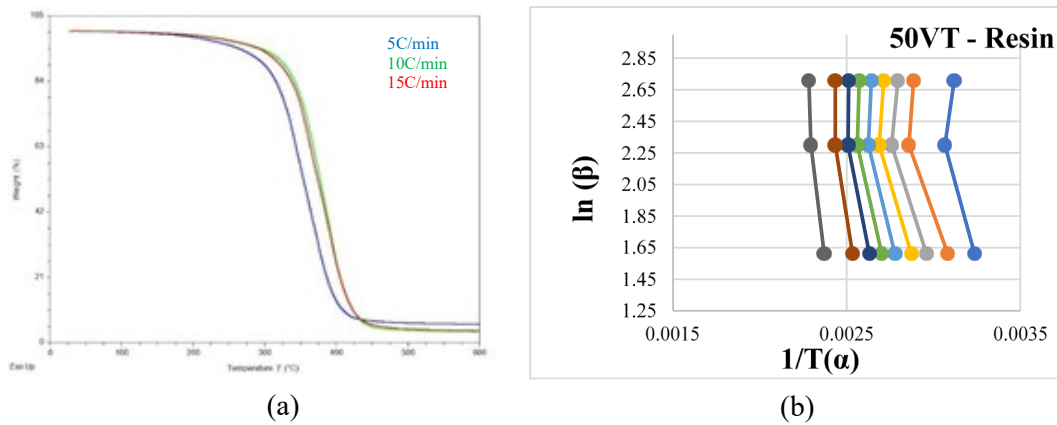


Figure 4.13: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 50VT – Resin

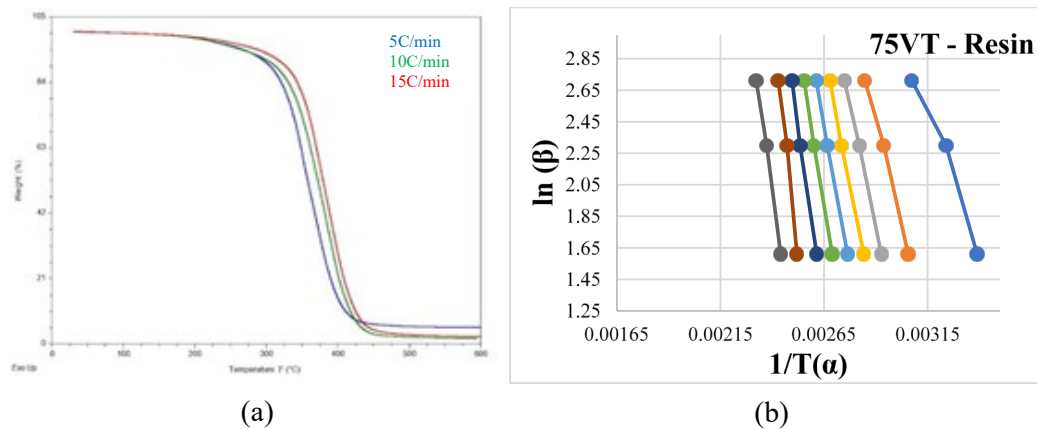


Figure 4.14: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 75VT - Resin

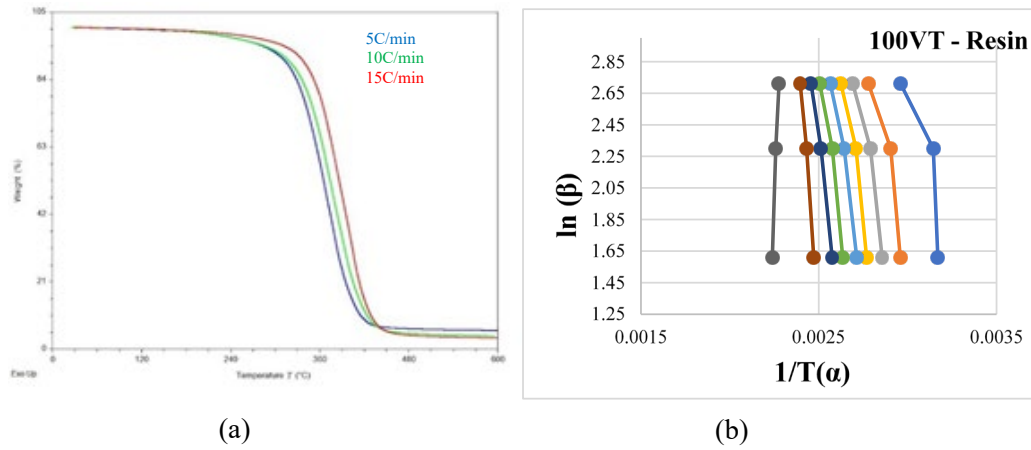


Figure 4.15: (a) TGA mass loss curve and (b) plot of logarithm of heating rate vs reciprocal temperature for conversion α from 0.1 to 0.9 for 100VT – Resin

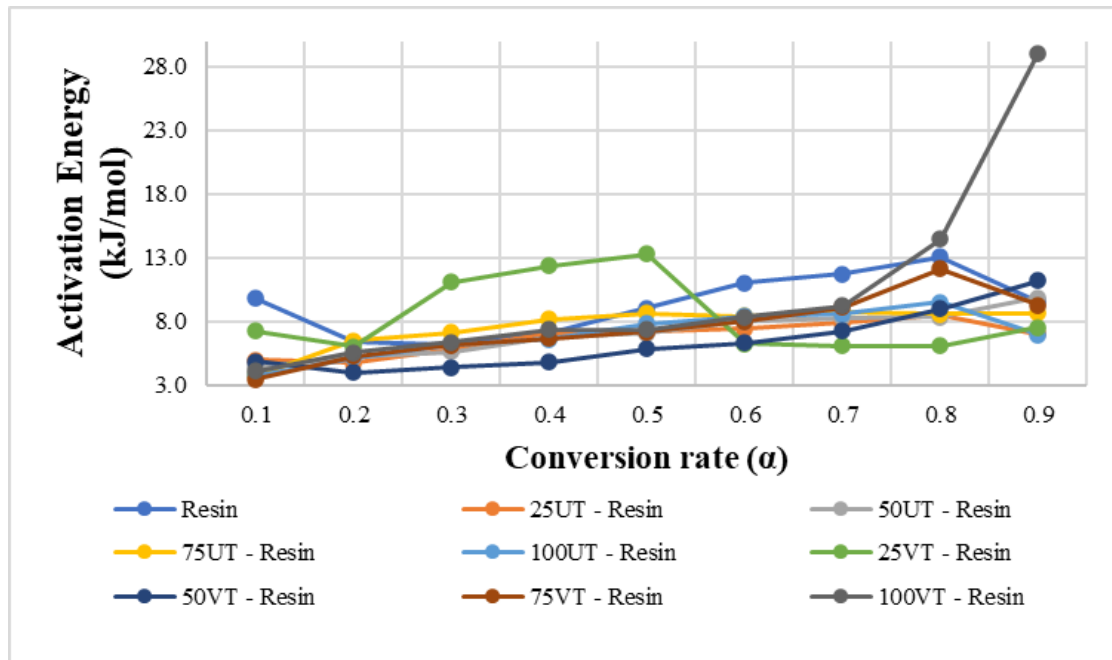


Figure 4.16: Activation energy versus conversion ratios for UT and VT - Resin according to Flynn-Wall-Ozawa method

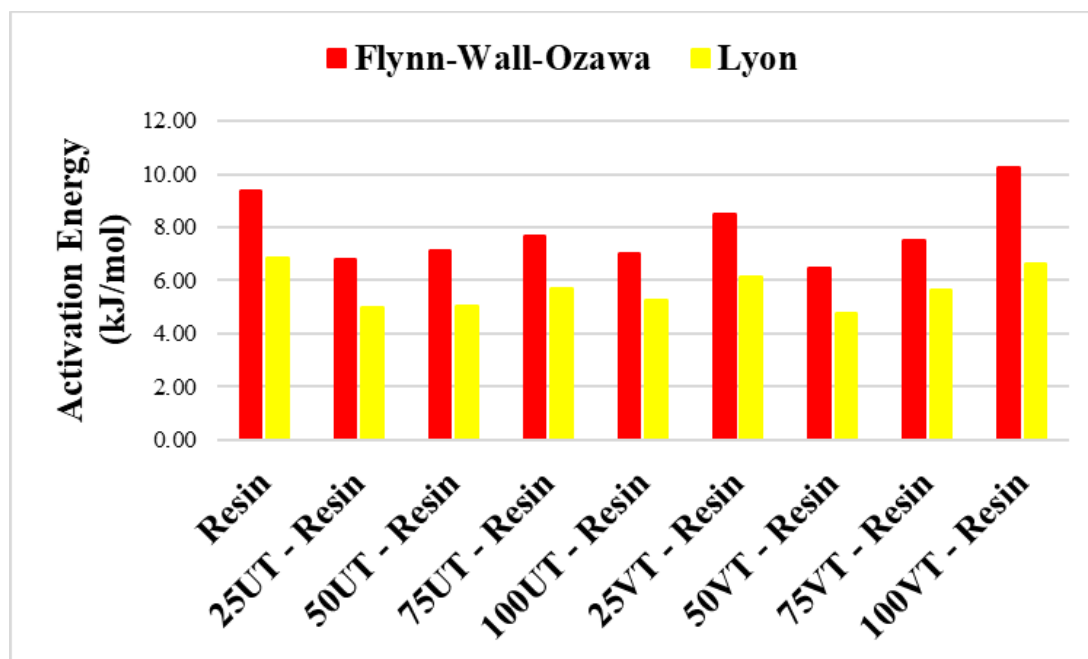


Figure 4.17: Comparison of activation energy for UT and VT - Resin according to Flynn-Wall-Ozawa and Lyon approximation method

From Figure 4.15 it was observed that there is a variation in activation energy values from low conversion rate to higher conversion rate. For resin systems, curing reaction happens before glass transition temperature and as conversion rate increase chemical controlled curing change into diffusion-controlled curing (de la Caba, Guerrero, Mondragon, & Kenny, 1998). Higher activation energies imply greater thermal stability and from activation energy calculations it was observed that at 1wt% vinyl silane treated alumina nanofiber loading level showed higher thermal stability. It was observed that degradation mechanism changed with addition of alumina nanofibers and surface treatment. From Table 4.1, thermal degradation temperature range for 10% conversion is 307 °C – 313°C for untreated alumina nanofiber modified polyester, whereas this temperature range increased with addition of vinyl silane treated alumina nanofiber modified polyester and was observed to be 308°C – 327 °C. The degradation temperature range for 50% conversion is in range of 370°C - 374°C for untreated alumina nanofiber

modified polyester and 371 °C-380 °C for vinyl silane treated alumina nanofiber modified polyester. The curing process of unsaturated polyester resin is a complex mechanism often changing from curing to vitrification at higher conversion rate (Lem & Han, 1984; Monti, Puglia, Natali, Torre, & Kenny, 2011). Hence there is a large variation in activation energies observed when changing from chemical controlled curing to diffusion-controlled curing.

4.2.3 Differential scanning calorimetry

With research gaining interest in use of nanofillers in thermoset based polymer composites, role of nanoparticles in curing reaction is also gaining interest. Literature investigation showed that nanoclay and carbon nanofibers are only amongst wide range of nanofillers which were studied for their effect on cure kinetics of unsaturated polyester resin. Differential scanning calorimetry is one of the popular techniques in understanding curing process of polymers although it does not give any information of chemistry associated with reaction.

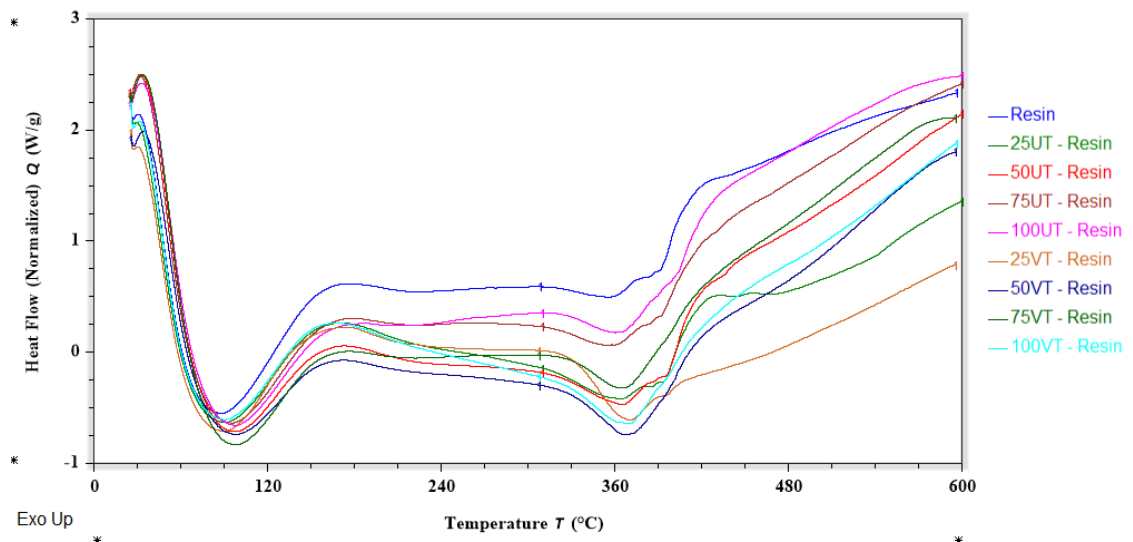


Figure 4.18: DSC scans of UT and VT - Resin.

Table 4.2: Summary of properties from DSC scans

Category	Glass transition temperature		Peak Temperature		Degree of cure	
	UT - Resin	VT - Resin	UT - Resin	VT - Resin	UT - Resin	VT - Resin
0	144.35		417.94		85.3	
25	145.87	138.15	424.37	371.18	79.5	86.7
50	147.13	148.20	422.61	418.33	81.3	94.7
75	147.10	146.01	421.98	418.08	79.6	83.6
100	147.57	145.01	430.31	429.58	80.1	83.8

Figure 4.17 represents DSC curves for all material systems and glass transition temperature, peak exothermic temperature, degree of cure is presented in Table 4.2. From literature studies and manufacturers recommendation the curing of polyester coupons is done at 80°C. The corresponding full cure heat capacity obtained from the literature is 336J/g. The degree of cure was obtained by using equation

$$\% \text{Cure} = 1 - \left(\frac{\delta H \text{ residual cure}}{\delta H \text{ full cure}} \right) \times 100 \quad 6$$

Glass transition temperature is associated with amorphous regions and has a significant effect on processing and physical properties of polymers. The segmental mobility during glass transition is associated with both flexibility of chains, as well as inter and intra molecular bonding in molecular chains. Additives, solvent residues, moisture, and other external parameters can affect glass transition temperature negatively, thus inhibiting curing. The glass transition temperature and percentage cure of nanocomposite as a function of alumina nanofiber content and surface treatment are represented in Figure 4.18a and 4.18b respectively. As observed from Figure 4.18a, addition of alumina nanofibers and surface treatment of alumina nanofibers do not have a degrading effect on glass transition temperature. The percentage cure in final nanomodified polyester decreased for UT - Resin, whereas percentage cure has seen an

increase in VT - Resin as observed in Figure 4.18b. The UT - Resin has almost same values for crystallinity and is less than the Resin. This can be explained by restrained space for crystalline growth caused by dispersed alumina nanofibers (M. K. Hossain et al., 2010). There could be a possibility of unreacted carbon double bonds remaining because of vitrification inhibiting cure percentage in untreated alumina nanofiber modified polyester systems.

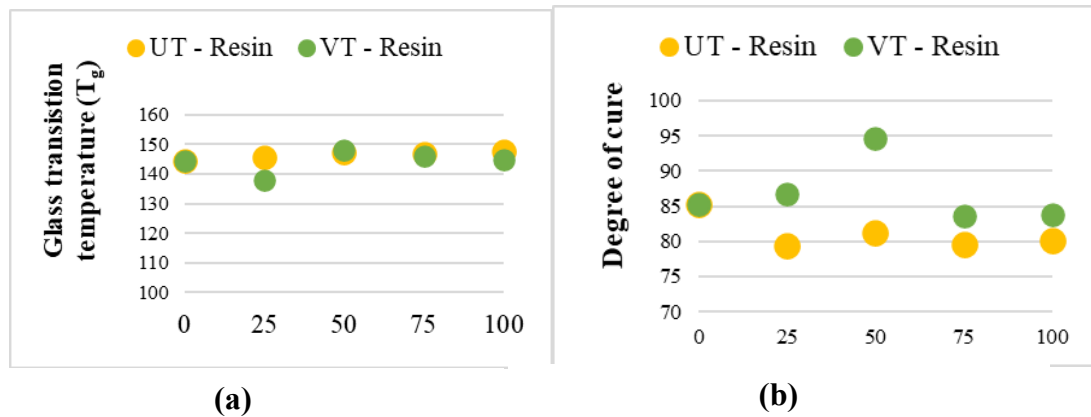


Figure 4.19: Variation in (a) glass transition temperature and (b) degree of cure for UT and VT - Resin

The reactive surface groups present on nanofillers provide by functionalizing using suitable surfactants results in nucleation sites which promote curing reaction thus attaining higher crystallinity. The higher mobility of double bonds and vitrification process occurring at higher conversion rates increasing activation energy as observed from TGA analysis causes decrease in unreacted double bonds making the system thermally stable. The curing reaction of polyester resin is quite complex and chains of polymer crosslink with each other according to styrene-polyester copolymerization, styrene-homo-polymerization and polyester homo-polymerization (Monti et al., 2011). Based on the understanding from (Lem & Han, 1984; Monti et al., 2011) in relation to cure studies on polyester resin system with styrene as reactive diluent, the first

exothermic peak represents styrene-polyester copolymerization and second peak refers to styrene homo-polymerization. Alumina nanofiber presence did not seem to influence type of polymerization reactive process occurring in nanocomposite system during crosslinking. Silane coupling agent used for surface treatment of nanofillers also have a dramatic effect on inhibition or promotion of amine functionalities present, which could participate in radical transfer reactions with peroxy radical or alkyl radicals affecting curing of polyester resin. In this case it is imperative that DSC scans alone cannot provide a sufficient understanding of chemical reactions happening during curing process to assess influence of functionalization or nanofiller.

4.3 Conclusions

Thermal stability of alumina nanofiber filled polyester nanocomposite systems was studied by using thermogravimetric analysis and differential scanning calorimetry analysis. Kinetic models which have been already applied for activation energy determination studies were utilized in this study. Based on thermal characterization studies the following conclusions were made.

1. The lower onset degradation ($T_{dec}(0.1)$) temperature and temperature at 50wt% mass loss ($T_{dec}(0.5)$) were enhanced with addition of VT-ANF to the Resin. The silane treated alumina nanofiber due to higher degree of crosslinking reactions with end groups of polyester resin impede propagation of decomposition reactions.
2. The improved interfacial interaction due to silane functionalization as observed from TEM images in chapter 2 resulted in reduced mobility of polyester around nanofillers, increasing thermal stability of nanocomposite. Styrene diffusion is

major contributor for mass loss in unsaturated polyester resin systems and nanofillers tend to trap diluents and inhibit movement of chains increasing crystallinity, thus contributing to good thermal stability.

3. The addition of alumina nanofibers did not show any deteriorating effect on thermal stability as compared to neat resin. However, since most of the thermal energy is converted into dissociation of bonds, VT -Resin showed reduced peak mass loss temperatures. Though not significant improvement, the improvement in $T_{dec} (0.5)$ temperature was observed for 25VT, 50VT and 100VT - Resin in the percentage of 2.6%, 1.22% and 1.77% respectively.
4. Activation energy is a measure of rate of chemical reaction and lower activation energy corresponds to higher reaction rate according to Arrhenius equation. Higher activation energies correspond to higher bond dissociation energies. Flynn-Wall-Ozawa and Lyons approximation methods predicted activation energy for alumina nanofiber modified polyester nanocomposite and incorporation of nanofillers nor surface treatment had a significant effect.
5. Differential scanning calorimetry scans used to determine glass transition temperature showed that addition of UT_ANF and VT_ANF to polyester resin did not have a deleterious effect.
6. The degree of cure as calculated from DSC scans for nine material systems revealed that silane treatment of alumina nanofibers improved extent of crystallinity. The inhibition of styrene evaporation due to silane agent is attributed to increased crystallinity and vitrification of the UT_ANF modified polyester leaving behind some unreacted double bonds is attributed for lower crystallinity.

However, since DSC scans does not provide any chemistry related evidence, no universal patterns for effect of vitrification or styrene evaporation inhibition can be deduced for the moment.

5. GLASS FIBER REINFORCED ALUMINA NANOFIBER FILLED POLYESTER COMPOSITES: LOW VELOCITY IMPACT CHARACTERIZATION

Laminated composite materials have found many applications in industry, defense, marine, transportation, automotive and energy sectors because of their attractive light weight and high stiffness-to-weight ratios. Despite their advantages, in-service impacts due to tool drops pose a greater threat which results in reduced residual strength leading to catastrophic failure. The classification of impact, velocity ranges and effects different parameters have been extensively reviewed and presented in chapter 1. Barely visible impact damage of impacted structures rises concern to imparted damage in composite, as it grows undetected in the structure. The huge delamination area results in stiffness loss and compressive strength of composite laminate structure. Several researchers have studied effect of reinforcement, effect of through thickness reinforcement, architecture type of reinforcement and addition of nanofillers on impact performance of respective laminates (Elias, Laurin, Kaminski, & Gornet, 2017; Kallagunta & Tate, 2019b; Landowski, Strugała, Budzik, & Imielińska, 2017; Pankow, Salvi, Waas, Yen, & Ghiorse, 2011; A. S. Rahman, Mathur, & Asmatulu, 2018; Singh, Nanda, & Mehta, 2017). The composite structure response to low velocity impact damage is through various damage mechanisms and an array of interaction of damage mechanisms making it difficult to assess impact strength of composite material. Fracture through matrix cracking, fiber breakage, fiber matrix debonding and delamination leading to damage of composite laminates, directly affecting residual compressive strength

(Johnson & Holzapfel, 2006; Kostopoulos, Baltopoulos, Karapappas, Vavouliotis, & Paipetis, 2010).

Woven glass fiber polyester composites owing to their ductile nature, when compared to brittle epoxy-based composites offer good impact resistance. In this study, impact strength of fourteen-layer 0/90 woven E-glass fabric reinforced polyester composites modified with alumina nanofibers are studied. One set of composites were modified with untreated alumina nanofibers and second set were modified with vinyl silane coupling (organic content 6-7%) agent treated alumina nanofibers. For a uniform distribution in polymer matrix, better wettability and interaction, surface energy of fiber should be close to surface energy of the polymer. Loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% were used for both sets of composites laminates. The glass polyester composites modified with untreated alumina nanofibers are here from referred to as UT-Composite and composites modified with vinyl silane treated alumina nanofibers as VT-Composite. Benzoyl Peroxide acquired from Sigma-Aldrich is used as curing agent with heat as external simulator. The alumina nanofiber dispersion into unsaturated polyester resin is as per processing conditions described in chapter 2. The composite laminates were prepared using manufacturing procedure as described in chapter 3.

5.1 Fiber volume fraction

The major disadvantage of using layup process is it induces voids in final composite material and addition of nanoparticles can worsen the quality since polymerization is affected by nanofillers. It is of high importance to assess fiber volume fraction of final laminate, since percentage of fiber content has a direct effect on the mechanical properties. Higher void content usually means greater susceptibility to

moisture absorption and weathering and increased variation or scatter in strength properties.

The fiber volume fraction was obtained using ASTM D3171 standard, which specifies use of one sample, having a cuboid shape with minimum surface area of 625mm². The sample was conditioned at 25C, at a relative humidity of 50% using procedure G from the standard. The density of specimen is determined according to ASTM D792 standard. The specimen is then placed in a desiccated crucible and is then placed in muffle furnace. The furnace is then heated up to 650C for 6h. The furnace is cooled to room temperature after the cycle and weight of specimen in holder is recorded. At specified temperature, polyester matrix is completely combusted, leaving the reinforcement. Using equations specified below, constituent material contents in the composite are calculated.

Fiber volume fraction

$$V_f = \left(\frac{M_f}{M_i} \right) \times 100 \times \frac{\rho_c}{\rho_f}$$

Matrix volume fraction

$$V_m = \left(\frac{M_i - M_f}{M_i} \right) \times 100 \times \frac{\rho_c}{\rho_m}$$

Void volume fraction

$$V_v = 100 - (V_f + V_m)$$

M_i = Initial mass of specimen, grams

M_f = Final mass of specimen after combustion, grams

ρ_c = Density of composite specimen, g/cm³

ρ_f = Density of reinforcement, g/cm³

ρ_m = Density of matrix, g/cm³

The overall constituent volume fractions are given in Table 5.1. It was observed that increase in void content is observed with addition of alumina nanofibers. Though there is an increase in void content with surface treated alumina nanofiber modification, void content is less as compared to untreated alumina nanofiber modification. The samples tested in this category for fiber volume and void volume fraction consisted of fourteen layers of woven glass fabric used for low velocity impact testing and is an average of five test samples used for mechanical testing.

Table 5.1: Overall constituent volume fraction of UT and VT – Composites

Sample	Density	Fiber Volume Fraction	Matrix Volume Fraction	Void Volume Fraction
	g/cc	V_f	V_m	V_v
Composite	1.98	57.9	40.0	2.1
25UT – Composite	2.00	63.5	30.5	6.0
50UT – Composite	1.98	62.5	30.7	6.8
75UT – Composite	2.02	67.2	24.8	8.0
100UT – Composite	2.00	66.8	23.6	9.5
25VT – Composite	2.01	61.9	34.4	3.6
50VT – Composite	2.02	64.3	30.8	4.9
75VT – Composite	2.04	66.6	27.2	6.2
100VT - Composite	2.00	66.1	25.1	8.8

5.2 Characterization

5.2.1 Low velocity impact

The impact test was performed according to ASTM D7136 standard for measuring damage resistance of fiber reinforced composite to a drop weight impact. CEAST 9340 drop tower impact test system as shown in Figure 5.1, which houses impactor and provision for varying load is used to perform the tests. The height of impact can be varied giving us necessary energy levels required to study composite laminate behavior. The transient behavior of rectangular samples with dimensions of 150mm x

100mm (length x width) with an average thickness of 7 ± 0.3 mm include deflection, load, and energy as a function of time.

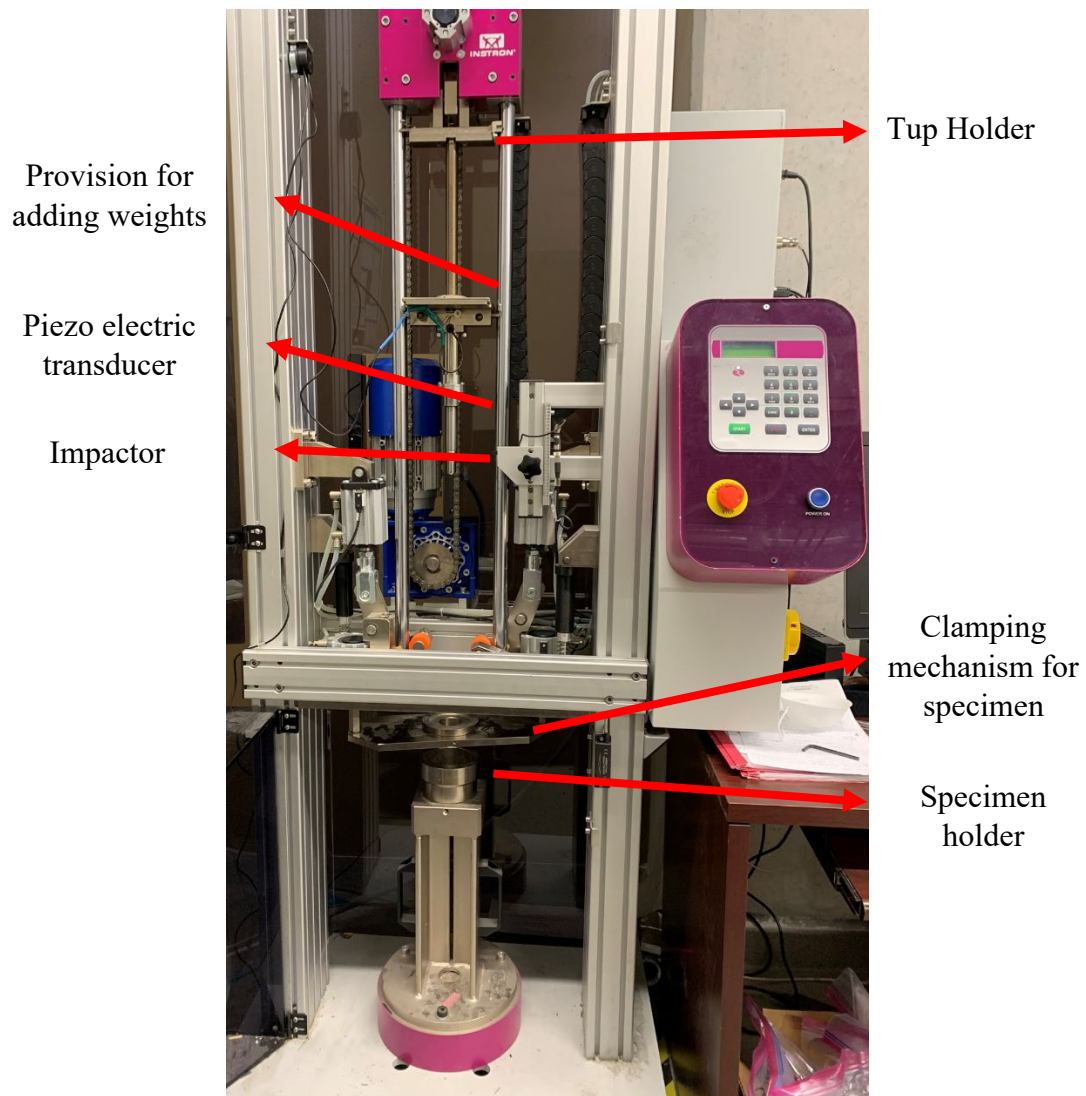


Figure 5.1: Drop tower low velocity impact test setup

The samples are impacted with a hemispherical impactor having a diameter of 12.7mm and having a drop weight of 22.568 kg. The impact tests were carried out by striking the samples at varying energy levels of 135J, 170J, 205J and 240J which are achieved by varying height of the impactor to 610mm, 768mm, 926mm and 1084mm, respectively. The extent of impact damage is predominantly dependent on magnitude of impact energies and hence mass is held constant and heights were varied for prescribed

energy values. The data is analyzed in terms of peak load and absorbed energy. The energy loss in damage creation under low velocity impact loading is explained by deformation in impact zone, matrix cracking, delamination and fiber breakage affecting structural behavior and residual vibrations of structure.

5.3 Results and discussion

Since, damage generated in composite laminate under low velocity impact loading can grow without any detection, load-displacement curve can be used in assessing residual strengths and damage in laminate. The changes/irregularities in ascending portion of curve before it reaches peak load, gives information about matrix cracks and first occurrence of delamination (primary damage mode) in composite laminate (M. E. Hossain, Hossain, Hosur, & Jeelani, 2014). The presence of matrix cracks does not have a significant effect on stiffness of laminate, but act as initiation points for delamination and fiber breaks which can dramatically change stiffness of laminate. The asymmetry of loading (ascending) and unloading (descending) curves is an indication of impact energy absorption by laminate. If the curves show a symmetry to peak load, it indicates that samples underwent localized damage and are not subjected to their full potential(M. E. Hossain et al., 2014). The change in slope of curves before reaching maximum load gives information about introduction of damage in laminate indicating change in stiffness. The displacement at the peak load is an indication of damage progression in the laminate, which is obtained from load-displacement plots. Hence, a load-displacement plot under low velocity impact event calculations can yield qualitative results such as introduction of damage, major damage onset, stiffness of laminate, energy absorption of laminates. In events where impact energy and absorbed

energy of laminate are equal during testing, load-displacement curves can yield results on onset delamination and perforation.

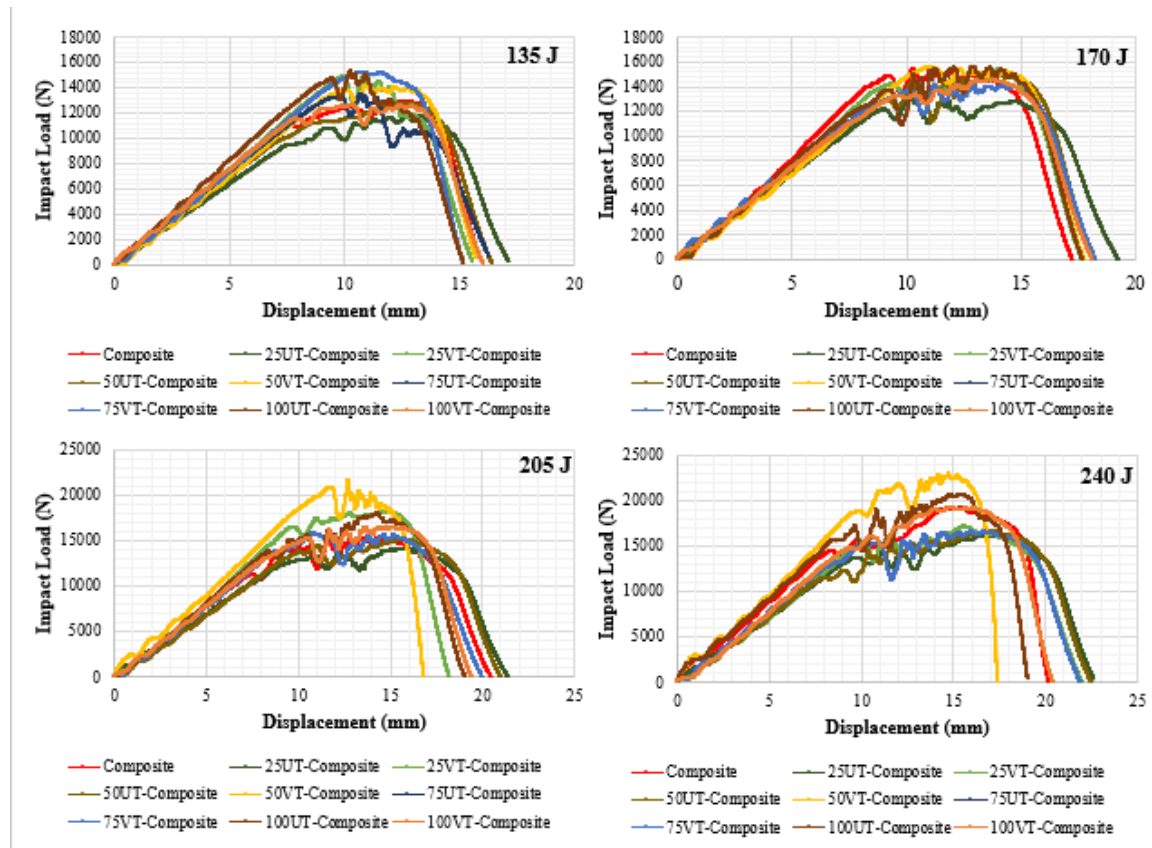


Figure 5.2: Impact load vs displacement plots of UT and VT – Composites at different energy levels.

Based on load-displacement curves mapped and as shown in Figure 5.2 at different energy levels of 135J, 170J, 205J and 240, none of the laminates show any symmetry of loading and unloading curves, which means energy absorption by laminate is significant. In all cases observed it can be implied that failure in composites is not due to penetration but due to matrix cracks, delamination, and fiber distortion. The addition of nanofillers have a significant effect on behavior of material to loading. As seen in Figure 5.2, at different energy levels, there is a variation in displacement before reaching peak load. Higher energy levels manifested higher impact loads on specimens. The

effectiveness of load transfer in composites as visualized in loading curve before attaining peak load indicates role of alumina nanofibers and surface treatment. Based on data obtained from load-displacement curves, the peak load values and stiffness values were calculated and are presented in Table 5.2.

Table 5.2: Summary of properties obtained from load-displacement curves

	Peak Load (kN)				Displacement at Peak Load (mm)				Stiffness (kN/mm)			
	135J	170J	205J	240J	135J	170J	205J	240J	135J	170J	205J	240J
0	12.9	15.4	15.4	19.1	12.7	11.1	11.6	15.4	1.5	1.6	1.5	1.8
25UT	11.7	13.2	14.1	16.1	13.4	10.1	15.6	16.5	1.3	1.4	1.4	1.4
50UT	12.7	15.0	15.1	16.6	12.9	13.9	15.5	17.2	1.4	1.4	1.4	1.4
75UT	13.5	14.1	15.8	16.6	10.7	11.2	10.8	16.0	1.5	1.5	1.5	1.5
100UT	15.3	15.6	18.0	20.6	10.3	12.9	14.3	15.5	1.6	1.5	1.6	1.8
25VT	14.8	15.3	18.1	17.1	9.9	14.0	14.7	15.6	1.5	1.5	1.6	1.6
50VT	14.2	15.5	21.5	22.9	10.9	10.9	12.7	14.8	1.4	1.4	1.8	1.9
75VT	15.2	16.2	20.8	22.3	10.6	13.2	11.6	15.2	1.5	1.58	1.9	2.0
100VT	12.6	14.5	16.4	19.2	10.3	13.6	15.0	14.9	1.5	1.4	1.6	1.6

Figure 5.3 represents interaction plots for peak load against alumina nanofiber loading level with and without surface treatment. The parallelism of lines determines if there is interaction between predictors for a particular response. If lines are parallel, then there is no interaction between predictors. If there are no parallel line, it indicates that interaction between predictors is significant. At all energy levels tested, vinyl silane treatment proved to be effective in attaining peak loads up to 0.75wt% loading level. Efficient transfer of stresses between silane treated alumina nanofiber, polyester resin and glass fibers resulted in higher peak loads attained for composites. At lower energy levels of 135J and 170J, 75VT -Composite are showed better results for peak load as observed in figure 5.3. At higher energy levels 205J and 240J, a further lower loading of 50VT – Composite resulted in higher peak loads attained. As shown in figure 5.4, average initial

slopes of load-displacement responses for samples at different loading levels and surface treatment for all energy levels are plotted. The samples showed variation in stiffness values and effect of surface treatment is more pronounced in the plots. It was observed that at lower energy levels, the effect of surface treatment at 0.25wt% loading levels manifested higher stiffness, which can be attributed to matrix strength increase by addition of nanofillers. However, at higher energy levels 0.75wt% loading level with surface treatment showed a major distinction in stiffness values. Depending on energy levels, energy absorption in composite may change from indentation to transverse matrix cracks to displacements due to stress wave propagation (Zhou & Davies, 1995). All the above factors lead to localized delamination or three-dimensional complex damage involving multiple delamination. The impactor displacement results in both the deflection of plate and local indentation to absorb introduced damage. In thick laminates, in-plane flexural stresses are of approximately the same order as normal stress component, so the deviatoric stress responsible for short beam failure is therefore relatively small (Davies, Hitchings, & Ankersen, 2006; Davies & Zhang, 1995), hence the impact energy is absorbed by the specimen typically as inelasticity or damage, but not complete perforation.

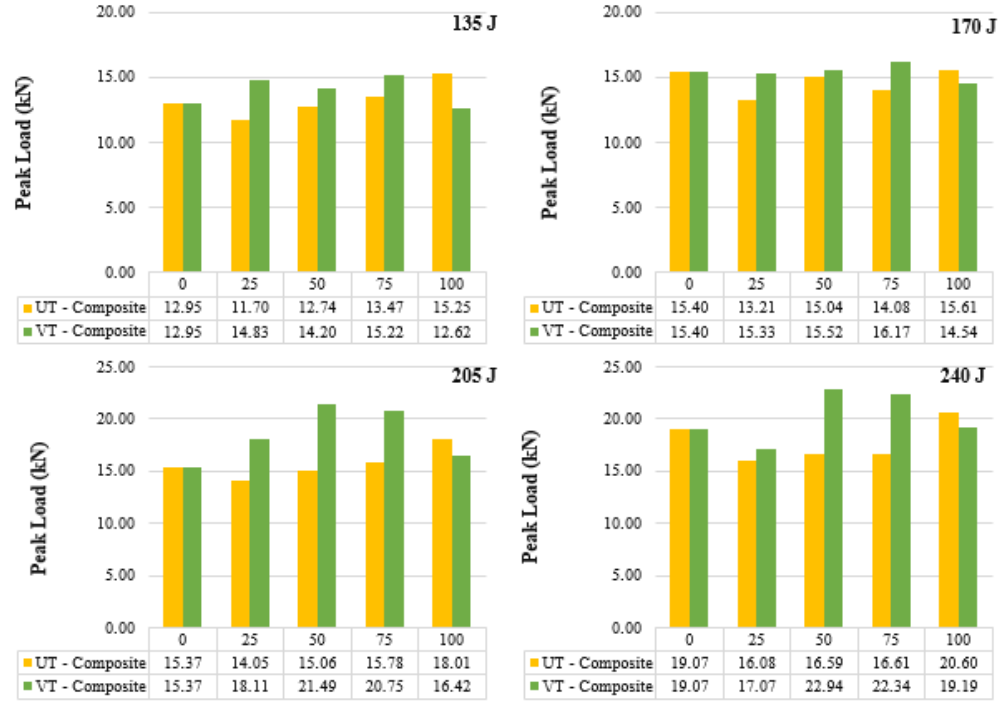


Figure 5.3: Peak load response of UT and VT - Composites at different energy levels.

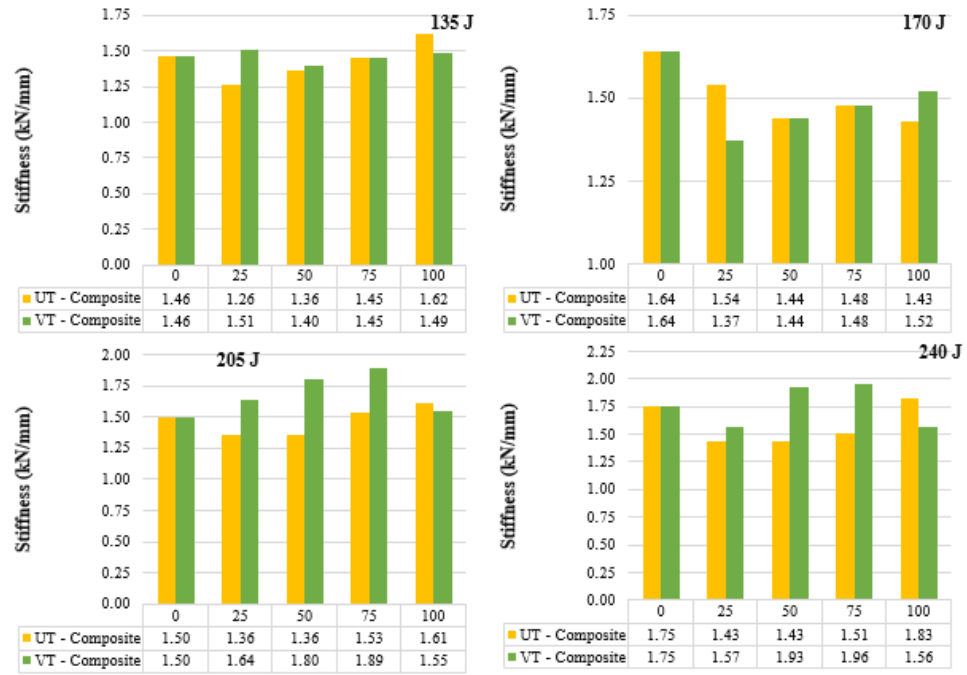


Figure 5.4: Stiffness response of UT and VT – Composites at different energy levels.

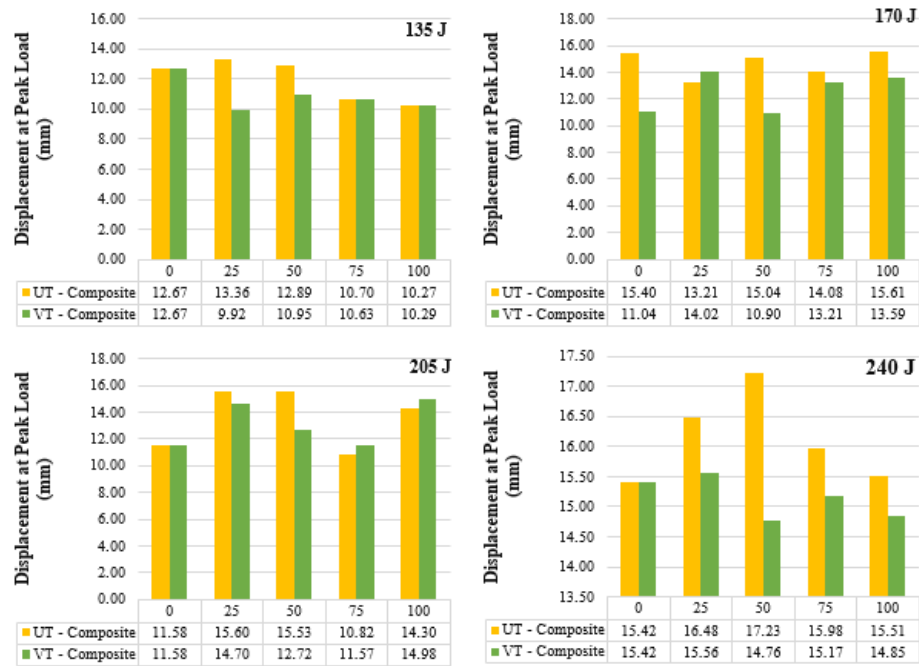


Figure 5.5: Displacement at peak load response of UT and VT – Composites at different energy levels.

Based on interaction plots as in Figure 5.3-5.5, there is a significant effect of alumina nanofibers and surface treatment on peak load attained, stiffness and displacement at peak load. A look at plots corresponding to peak load values and displacement at peak load values as in Figure 5.3 and figure 5.5, the displacement in composites is in proportion with variation in peak load. The efficient stress transfer between toughened matrix and fiber resulted in higher displacement of specimen, indicating effect of nanofillers in restricting damage growth before attaining a peak value. However, stiffness values did not follow the trend corresponding to peak load. The voids present in composites because of manufacturing procedure resulted in dramatic variation in stiffness values. Nanofillers, tend to increase stiffness of composites by providing a torturous path for cracks generated before reaching a critical value.

The transient responses including load and energy vs time were plotted as shown in Figure 5.6-5.14. It was observed that with increasing energy levels, the peak load

manifested in composites increased. It was observed that there were oscillations in the graphs before reaching maximum value. The significance of oscillations are qualitative indications to realize the effect of alumina nanofibers and surface treatment on impact response (M. E. Hossain et al., 2014). The increase in impact load after these significant oscillations indicate redistribution of load to neighboring areas. The UT - Composite as compared with VT - Composite indicate extensive damage in composite before reaching maximum load. The time taken for first occurrence of damage and time taken to reach peak load are represented in Table 5.4. The absorbed energy which is difference between total energy and energy peak load represent energy spent in creating and propagating damage after reaching peak loads.

Table 5.3: Summary of properties as observed from energy vs duration curves

	Energy at Peak Load (J)				Total Energy (J)				Absorbed Energy (J)			
	135	170	205	240	135	170	205	240	135	170	205	240
0	103.1	94.6	93.3	176.5	132.5	167.1	199.0	248.9	29.4	72.6	105.7	72.4
25UT	98.1	68.7	140.3	162.6	126.7	161.7	197.1	236.1	28.6	93.0	56.8	73.5
50UT	101.3	124.6	142.5	175.7	130.8	168.2	200.3	236.2	29.5	43.6	57.7	60.5
75UT	80.6	89.1	87.4	164.9	130.0	167.2	200.0	236.9	49.4	78.1	112.6	71.9
100UT	83.6	115.1	145.1	191.3	134.4	168.3	204.5	245.2	50.7	53.5	59.4	53.9
25VT	73.6	132.4	162.1	156.5	133.4	168.3	205.7	235.6	59.7	35.9	43.5	79.0
50VT	82.0	83.6	143.9	195.9	134.8	168.4	211	245.7	52.7	84.8	67.1	49.7
75VT	83.0	12.7	127.0	205.7	136.0	168	210.1	245.5	52.9	155.2	83.0	39.7
100VT	75.3	120.7	151.7	158.9	131.8	164.9	203.0	240.9	56.4	44.2	51.2	82.0

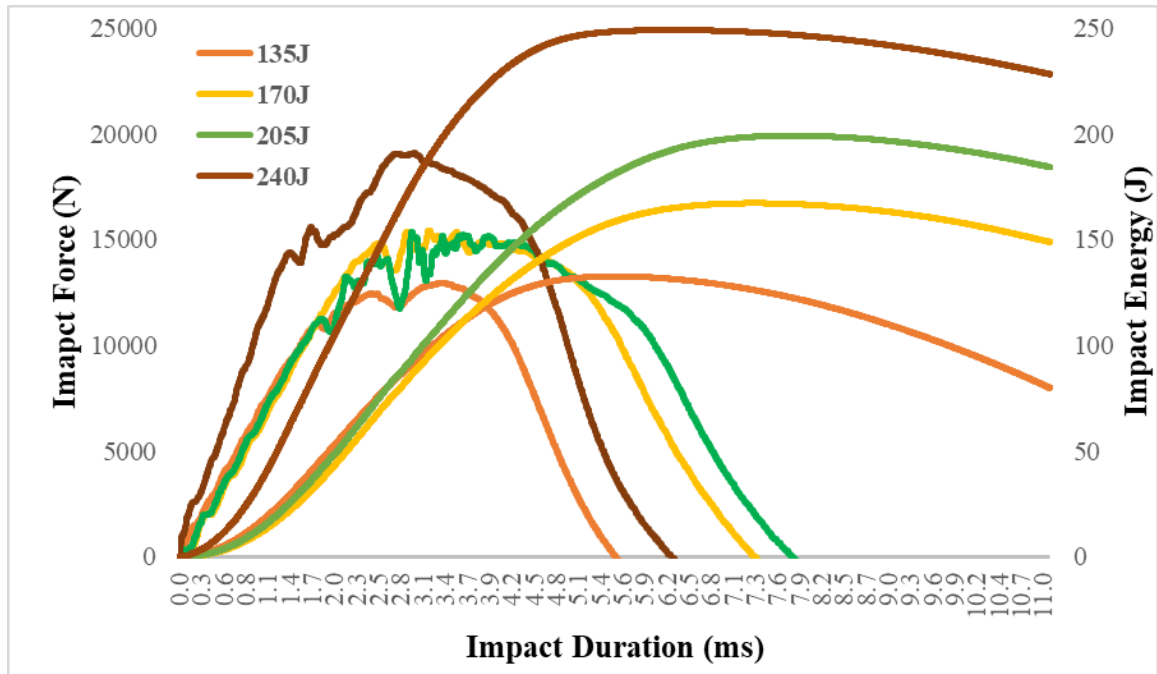


Figure 5.6: Impact load and energy vs duration response of Composite

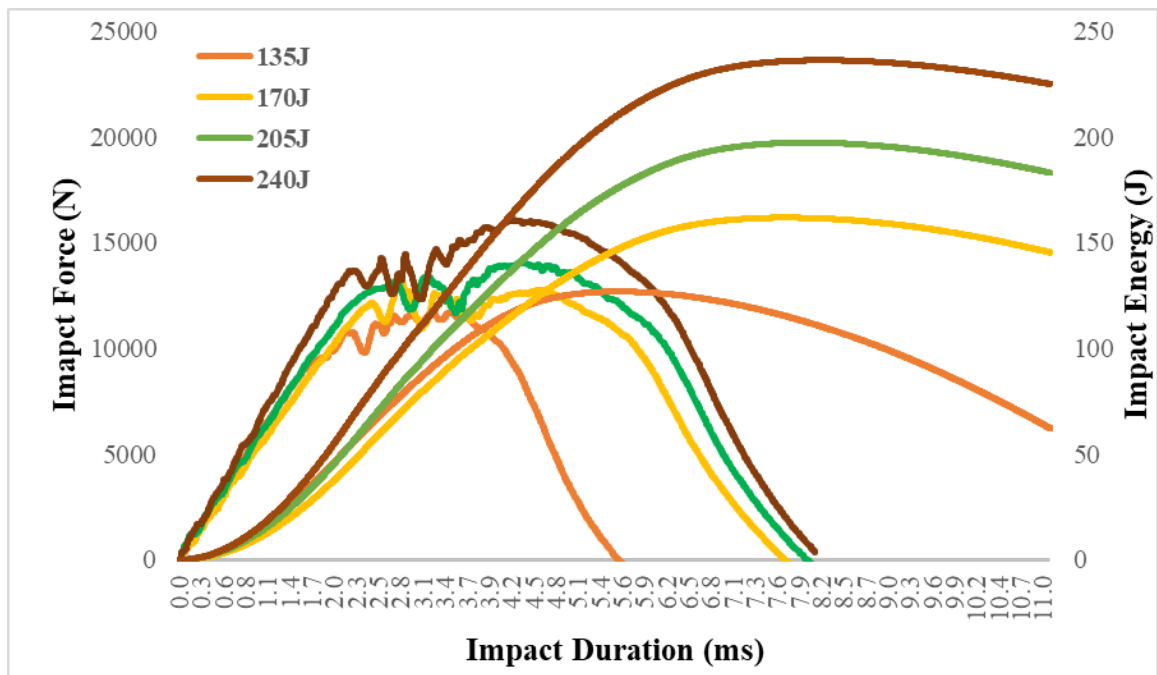


Figure 5.7: Impact load and energy vs duration response of 25UT - Composite

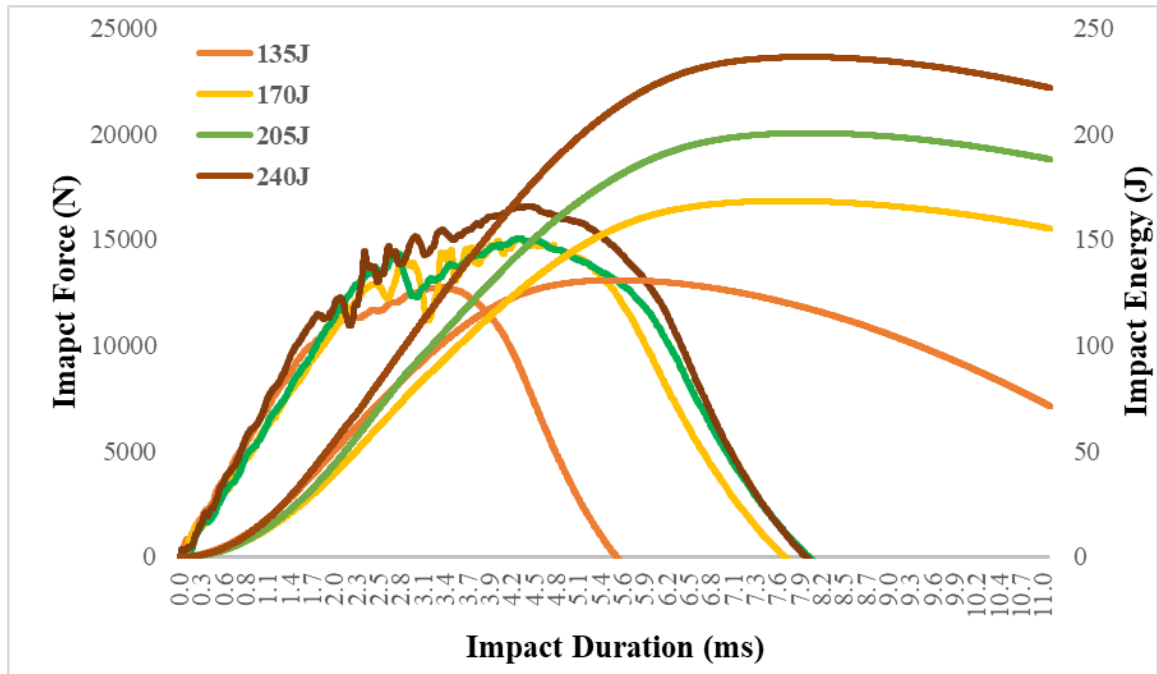


Figure 5.8: Impact load and energy vs duration response of 50UT - Composite

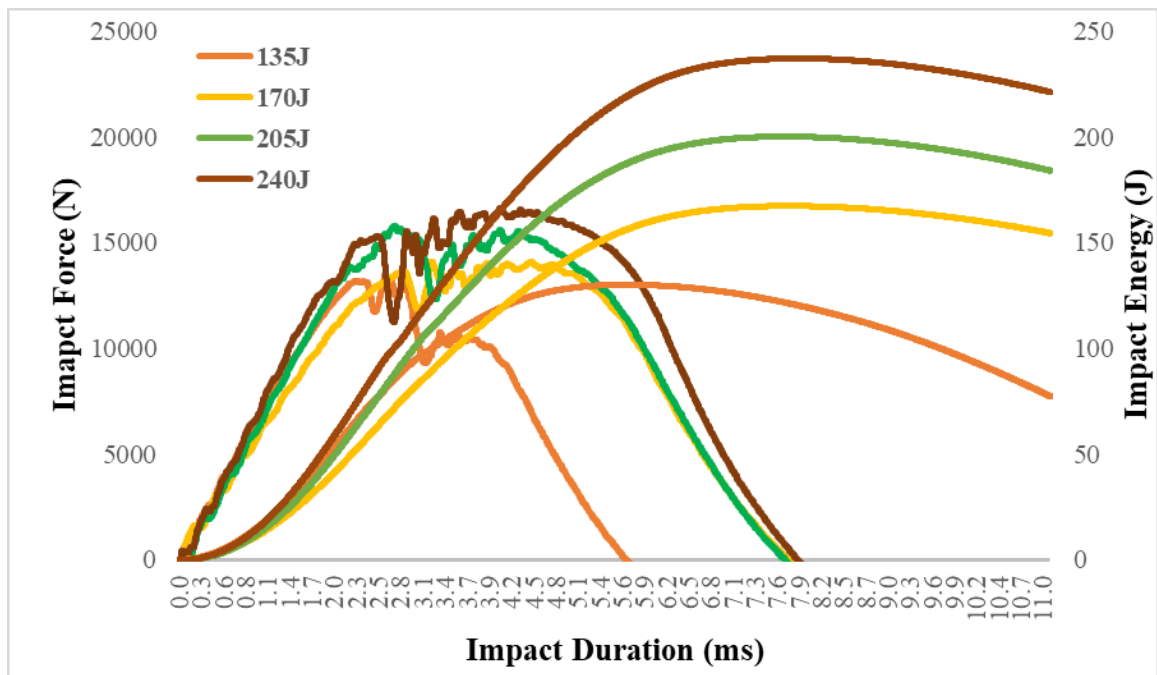


Figure 5.9: Impact load and energy vs duration response of 75UT - Composite

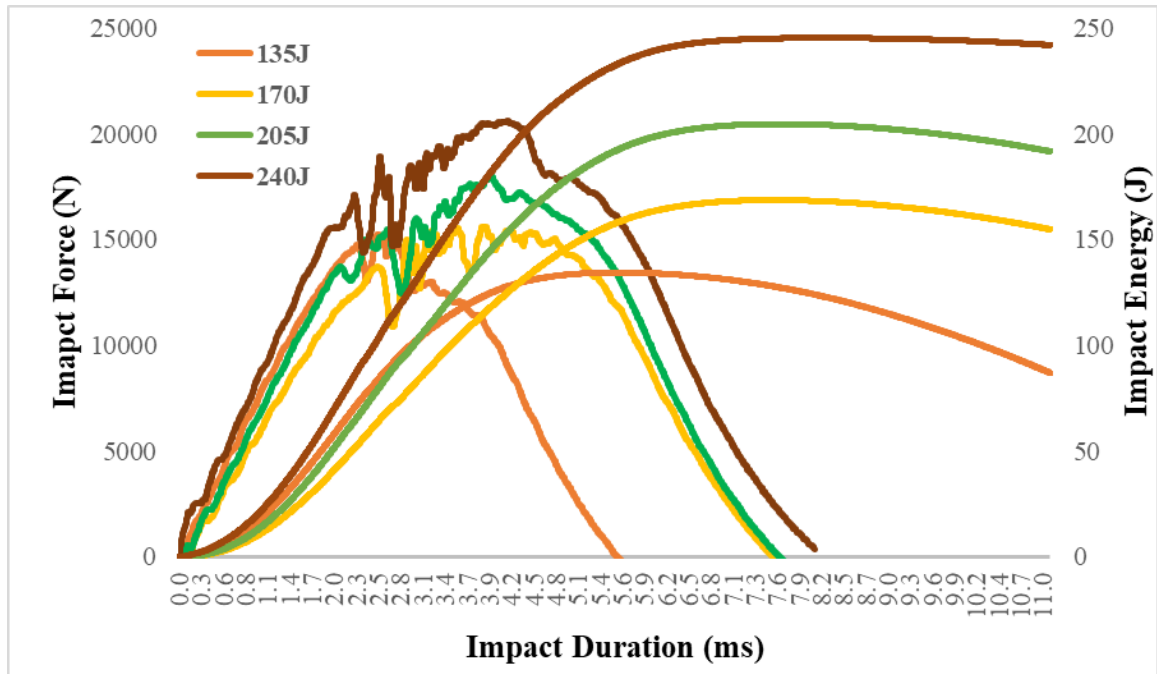


Figure 5.10: Impact load and energy vs duration response of 100UT - Composite

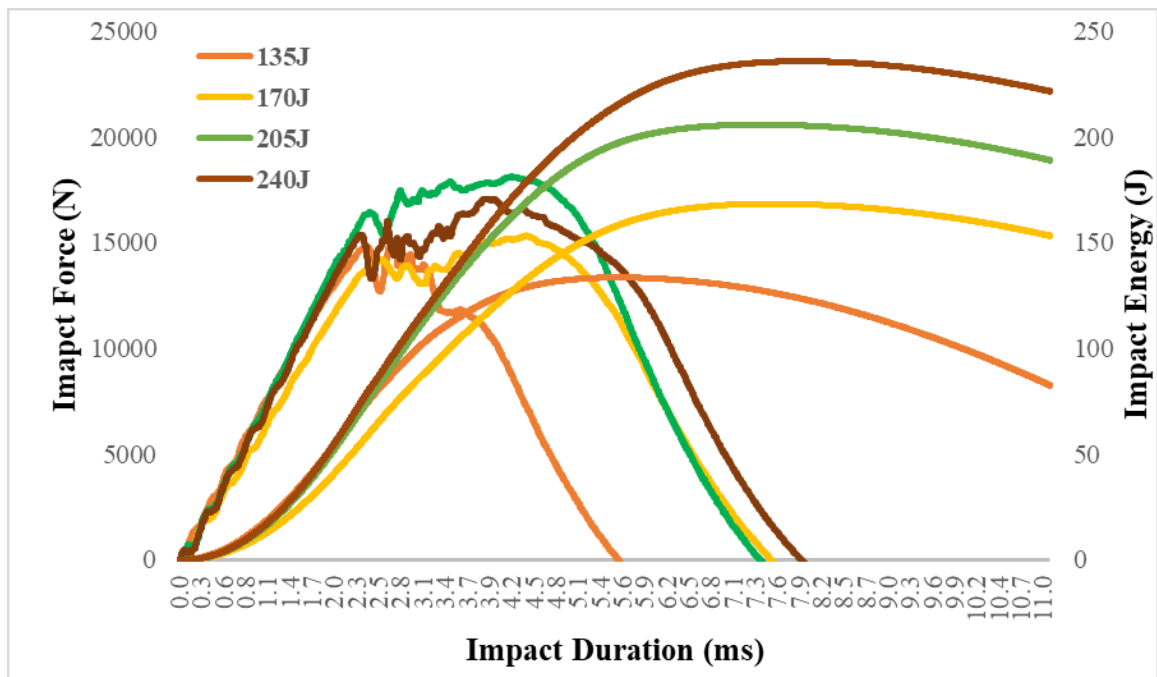


Figure 5.11: Impact load and energy vs duration response of 25VT - Composite

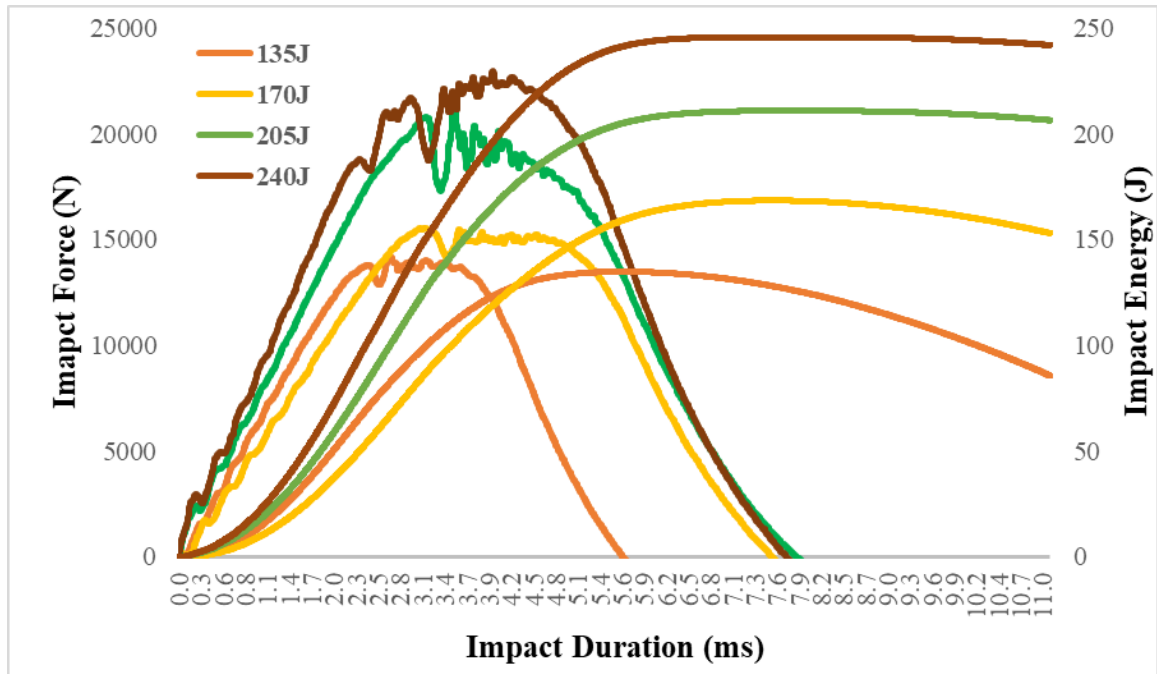


Figure 5.12: Impact load and energy vs duration response of 50VT - Composite

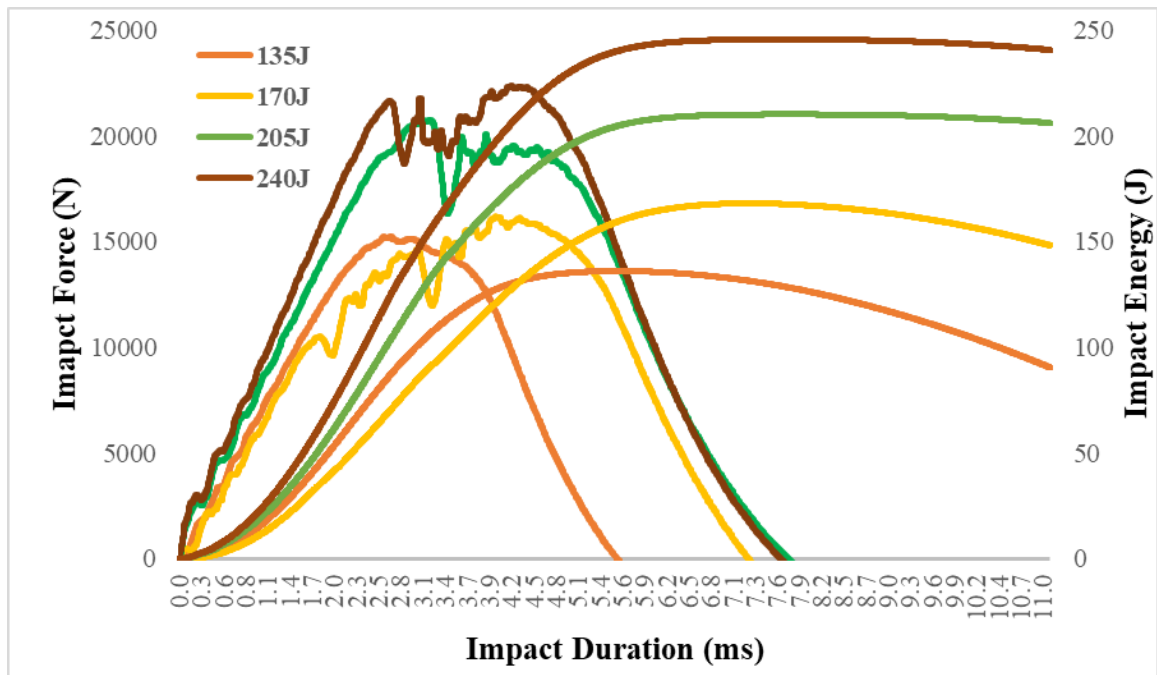


Figure 5.13: Impact load and energy vs duration response of 75VT - Composite

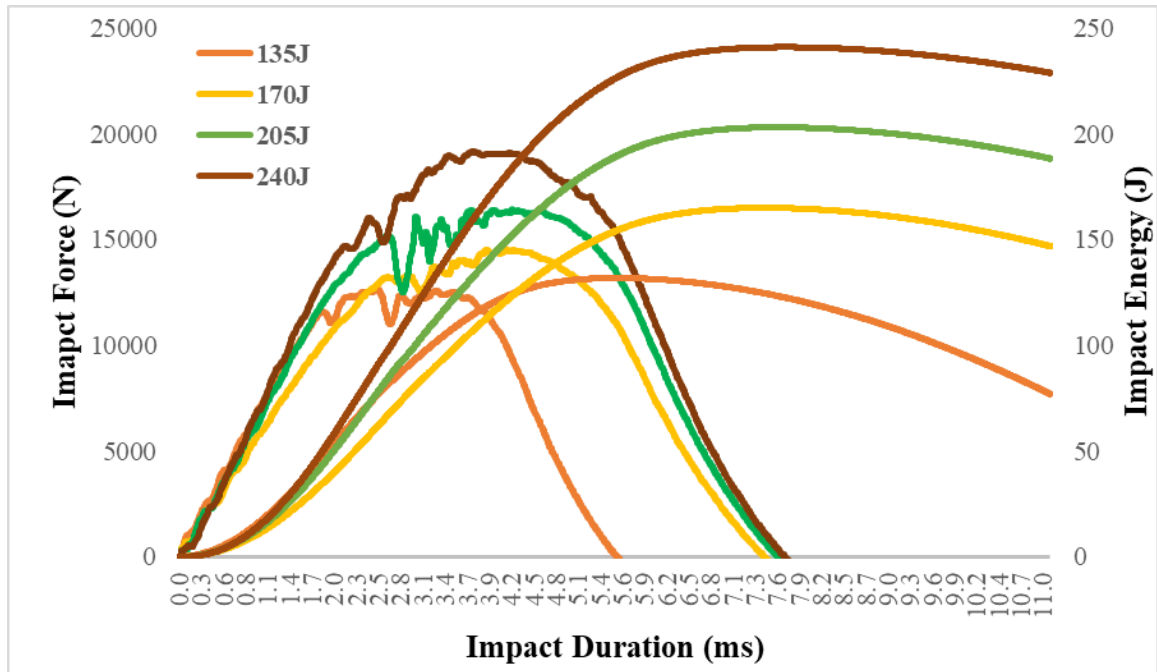


Figure 5.14: Impact load and energy vs duration response of 100VT – Composite

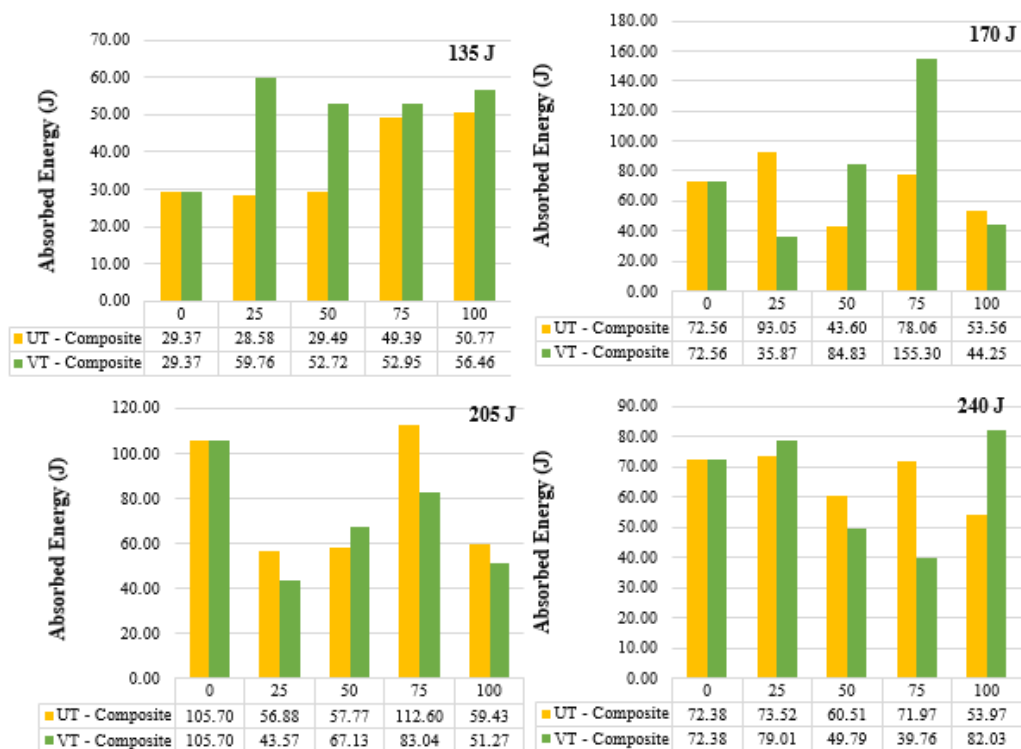


Figure 5.15: Absorbed energy of UT and VT – Composite at different energy levels

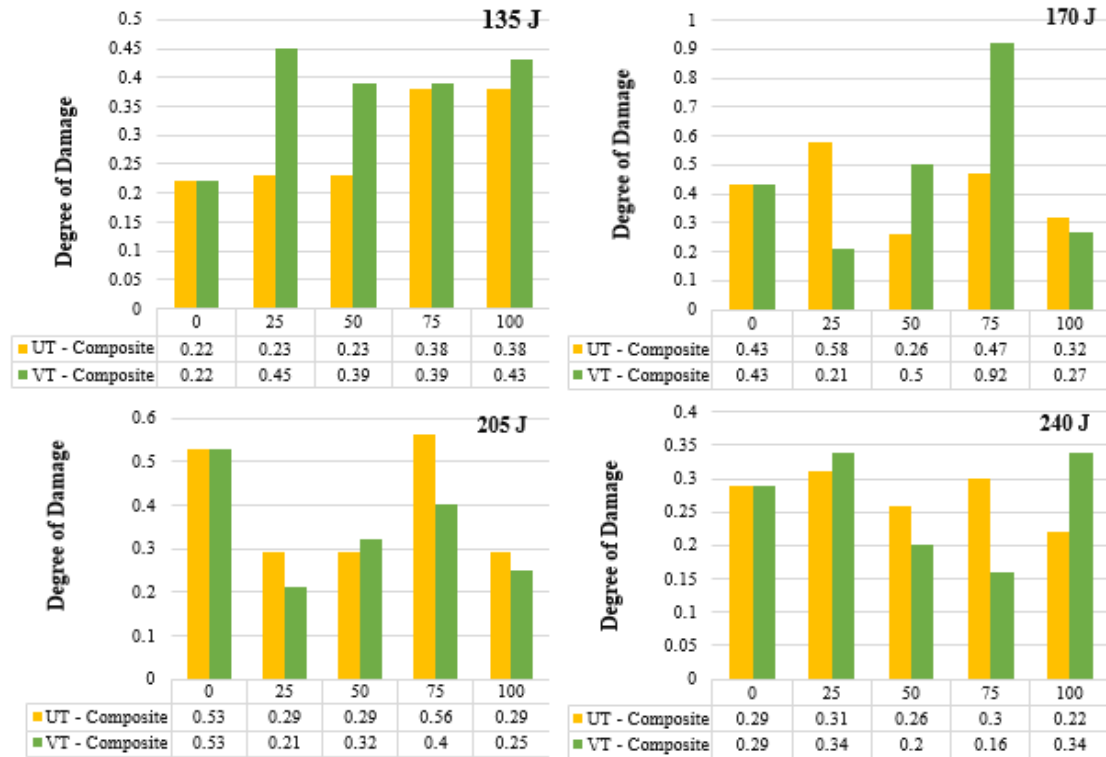


Figure 5.16: Degree of damage of UT and VT – Composite at different energy levels

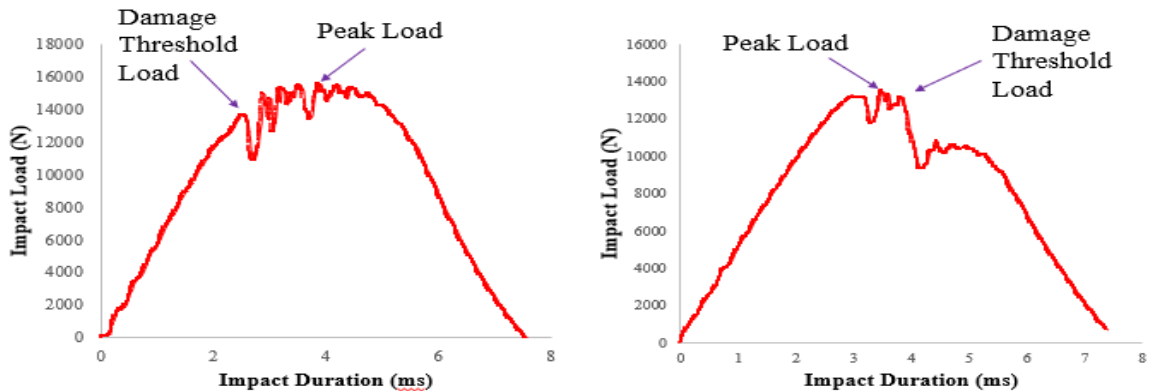


Figure 5.17: Representative image showing DTL obtained from load vs duration plot

The characteristic of woven composites under impact loading is no sharp load-drop after reaching maximum load as observed from load-deflection response, which indicates qualitatively that damage is not significantly high to cause penetration of composite (Baucom & Zikry, 2005). On the load-duration curve there exists a threshold load values, which represents onset of delamination. Schoeppner and Abrate, defined

sudden drop on loading curve is the significant damage event, indicating dramatic stiffness reduction and defined it as damage threshold load (as shown in Figure 5.17) (Schoeppner & Abrate, 2000). Matrix cracks do not have a significant effect on matrix stiffness it reaches maximum load. Hence it is suitable to determine delamination threshold load values which indicate significant damage event (predominantly delamination, but including fiber breakage, local puncture, or indentation). The values of damage threshold load and respective duration at which it occurred are calculated from curves plotted in Figure 5.6-5.14 and are reported in this study. Figure 5.15 and 5.16 represent absorbed energy and degree of damage due to impact. It was observed that VT - Composite showed greater values of absorbed energy and degree of damage is in proportion with absorbed energy for respective laminates. Matrix cracking, fiber matrix debonding and delamination are typically associated with matrix volume fraction and increase in matrix toughness by addition of nanofillers typically aids in higher energy absorption. The matrix cracks which are first damage absorption mechanism and initiation points of delamination propagate through resin rich regions. In case of alumina nanofibers modified composites, crack propagation was arrested due to presence of efficiently dispersed nanofillers. The better interaction between alumina nanofibers and vinyl silane coupling agent enhanced surface energy of nanofillers which furthermore aided in crack blunting thus contributing to higher energy absorption.

The tabulated values of damage threshold load, time taken to reach damage threshold load and time taken to reach peak load is shown in Table 5.4. As shown in table, VT - Composite showed close times when it reached peak loads and damage threshold load. The interaction between resin matrix and glass fibers was enhanced by

addition of vinyl silane treatment, which eventually resulted in increased interfacial interaction between layers resisting delamination. The surface treatment aided in efficient stress transfer by resisting cracks reaching the interfacial region before reaching peak load. Figure 5.18 represents damage threshold loads from respective force vs time plots which establishes increase in damage threshold load with addition of surface treated alumina nanofibers. When compared to UT - Composite, VT - Composite at 0.25wt% has seen increase by 37.8%, 16.2%, 25.6% and 9.01% at 135J, 170J, 205J and 240 J respectively. At 0.5wt% enhancement in DTL was noted to be -, 11.9%, 45.7% and 81.9% at 135J, 170J, 205J and 240J, respectively. At 0.75wt% enhancement reported to be 7.2%, 39.17%, 39.59% at 135J, 170J, 205J and 240J, respectively.

As represented, alumina nanofibers and surface treatment have a greater impact on how composites respond to incident low velocity impact. If damage threshold load is above peak load, then significant damage in composites do not occur before reaching peak load. However, if peak load occurs after damage threshold load, then significant damage has occurred in composite laminate before reaching the peak load. VT - Composite showed behavior where damage threshold loads, and peak loads occur simultaneously, or peak loads occur before reaching damage threshold load and in some cases, there is no damage threshold load indicating excellent residual strengths in the respective composite. The surface treated alumina nanofiber modified composites also showed increased times to reach damage threshold loads indicating effectiveness in energy absorption of composite.

Table 5.4: Time to reach peak load and DTL

	Damage Threshold Load (DTL) (kN)				Time to DTL (ms)				Time to Peak Load (ms)			
	135J	170J	205J	240J	135J	170J	205J	240J	135J	170J	205J	240J
0	12.3	14.6	13.7	-	3.4	2.6	2.7	-	4.4	3.2	3.0	4.0
25UT	10.5	11.9	12.8	13.8	3	2.5	2.8	2.6	4.6	2.8	4.4	4.2
50UT	-	13.7	14.1	11.8	-	3	2.8	2.1	4.5	4.3	4.3	4.5
75UT	12.9	13.2	14.7	15.2	3.2	2.9	3.1	2.6	3.5	3.2	2.7	4.1
100UT	14.5	13.5	15.3	16.5	3.1	2.6	2.7	2.3	3.4	3.9	4.0	4.2
25VT	14.6	13.9	16.2	15.1	3.2	2.6	2.5	2.4	3.2	4.4	4.2	3.9
50VT	13.7	15.3	20.5	21.4	3.3	3.3	3.2	2.7	3.6	3.1	3.5	4.0
75VT	-	14.2	20.6	21.3	-	3.1	3.3	2.7	3.5	4.0	3.1	4.2
100VT	12.4	13.0	15.0	15.8	3.4	2.9	2.7	2.5	3.4	4.2	4.2	3.7

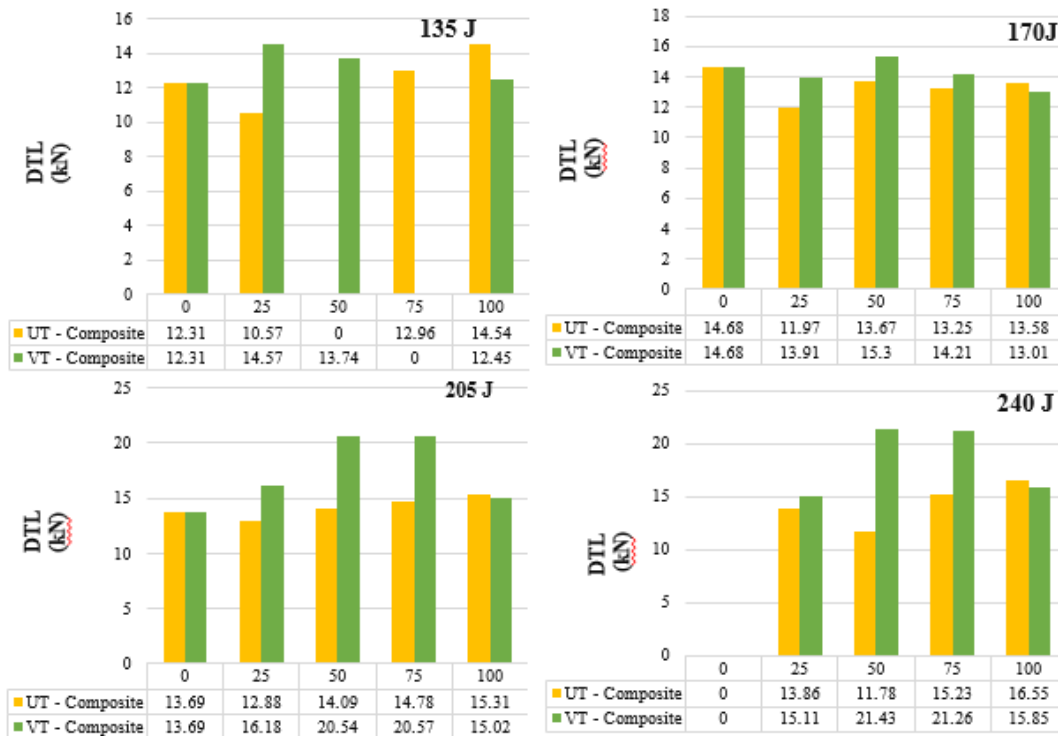


Figure 5.18: DTL of UT and VT - Composite at different energy levels

5.4 Post damage evaluation

Impact loading induces a complex series of failure modes including matrix cracks, surface micro-buckling, delamination, ply shear-out and fiber fracture often occurring as an interaction of all failure modes depending on incident impact energy. The load

bearing capability of composites are determined by elastic and inelastic energy absorption associated with composite response under total incident energy. Unless partial or complete penetration of laminates occur, energy absorption capability assessment is unlikely to be majorly influenced by matrix cracking, surface micro-buckling alone.

Figure 5.19 represents damage on impact side of control composite laminates at energy levels used for this study. It was observed that there are patterns on the impact side of the composite laminates which are caused more likely due to fiber being pulled by the impactor. In some cases, there were cracks observed which propagated outward from point of impact. In all the cases, there was significant indentation caused by the tip of impactor and as tip further tried to move into the composite, the fibers were pulled from surface. As can be observed from the back lit images, damaged portion turned from translucent to opaque which is due to heavy distortion of matrix and fibers during impact energy absorption. The damage area consisted of a circular region, which is due to circular clamp used. As energy level increased, damage progressed towards the edges where it was not confined, but major of energy was dissipated by energy absorption mechanism such as matrix cracking, matrix distortion and fiber distortion. No fiber breakage or penetration was observed in visually inspected laminates.

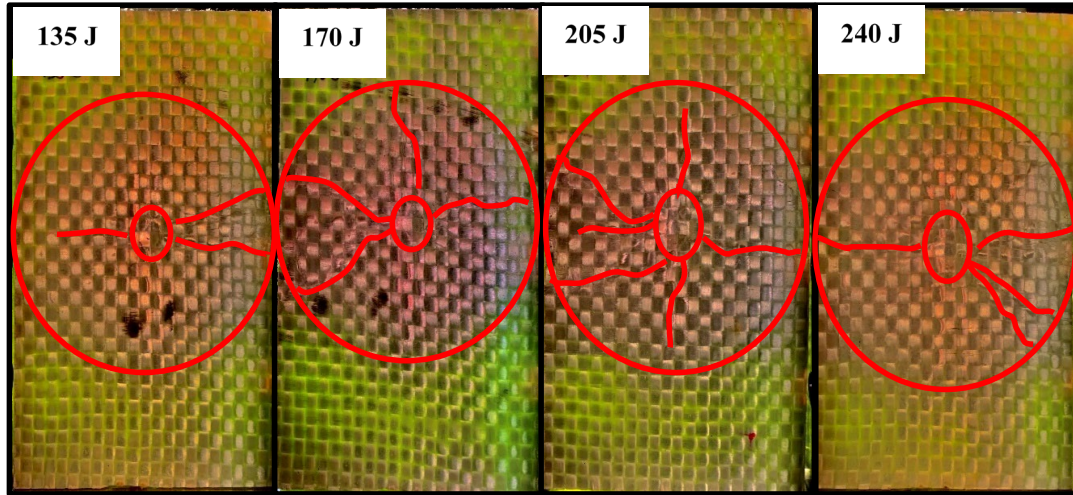


Figure 5.19: Damage spread in composites at different energy levels

Figure 5.20 and 5.21 represent damage caused by impactor on the side of impact and back side of composite respectively at 135J energy level. It was observed that, VT - Composite showed minimum primary/secondary yarn pulling as compared to UT - Composite indicating enhancement in inter layer strengths. The failure of yarns starts from the tip of impactor and the strain in primary yarns is significantly higher than secondary yarns. This causes a sequential failure of top layer yarns by pulling in direction of impactor and further continuing until tensile failure strain causing fiber breakage and penetration. Thus, damage is more concentrated around the point of impact and energy absorption by process of matrix cracking and delamination would continue until there is complete penetration. Hence, in our study as observed from images it is safe to say that major of the energy absorbed is through matrix cracking and delamination. From damage threshold load calculations VT - Composite attained higher damage threshold loads, hence from these observations it may be regarded as certain that surface treatment aided in efficient load transfer through the layers of the composite. The conical deformation on back face of composite is more relevant form of energy absorption in which incident

energy is absorbed by movement of primary yarns in path of impactor. The cone height formation during impact event is represented in Figure 5.22. Different loading levels of alumina nanofiber and surface treatment of alumina nanofiber at 135J, 170J, 205J and 240J observed cone formation without any perforation indicating incident energy was transferred into matrix cracking, delamination, and cone formation. Secondary yarn deformation in conjunction with primary yarn deformation results in greater cone heights as the secondary yarn volume is significantly higher than volume of primary yarns (Naik, Sekher, et al., 2016). Due to woven fiber architecture, there was no splitting of bottom layers observed as weave accommodates incident energy by fibers in both directions from failing (Baucom & Zikry, 2005).

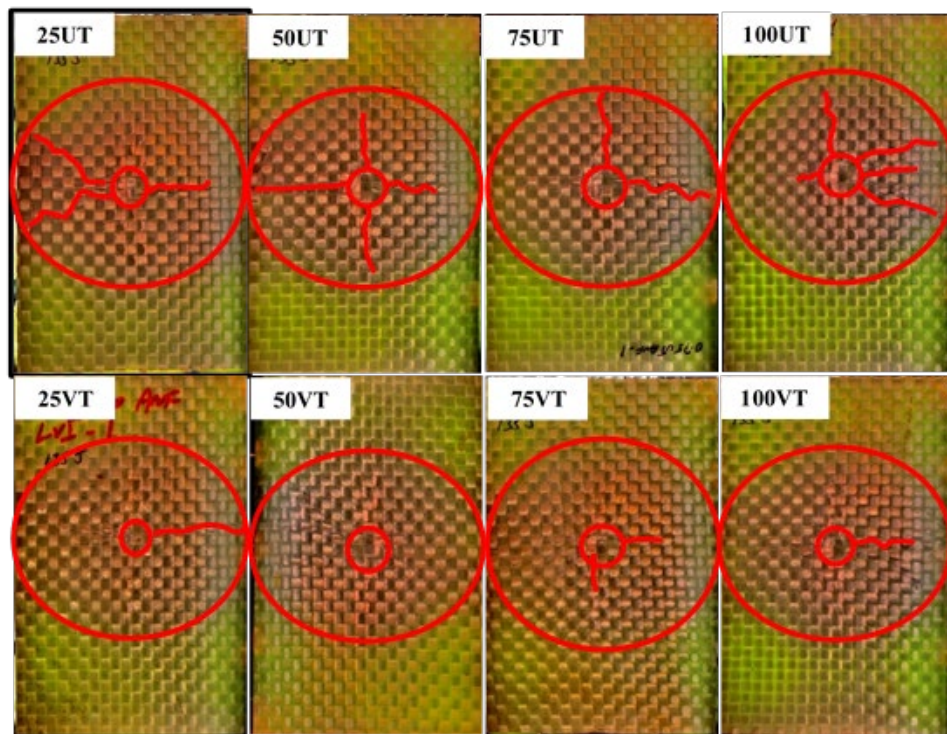


Figure 5.20: Impacted side images showing damage spread and propagation of damage in composites at impacted energy level of 135J

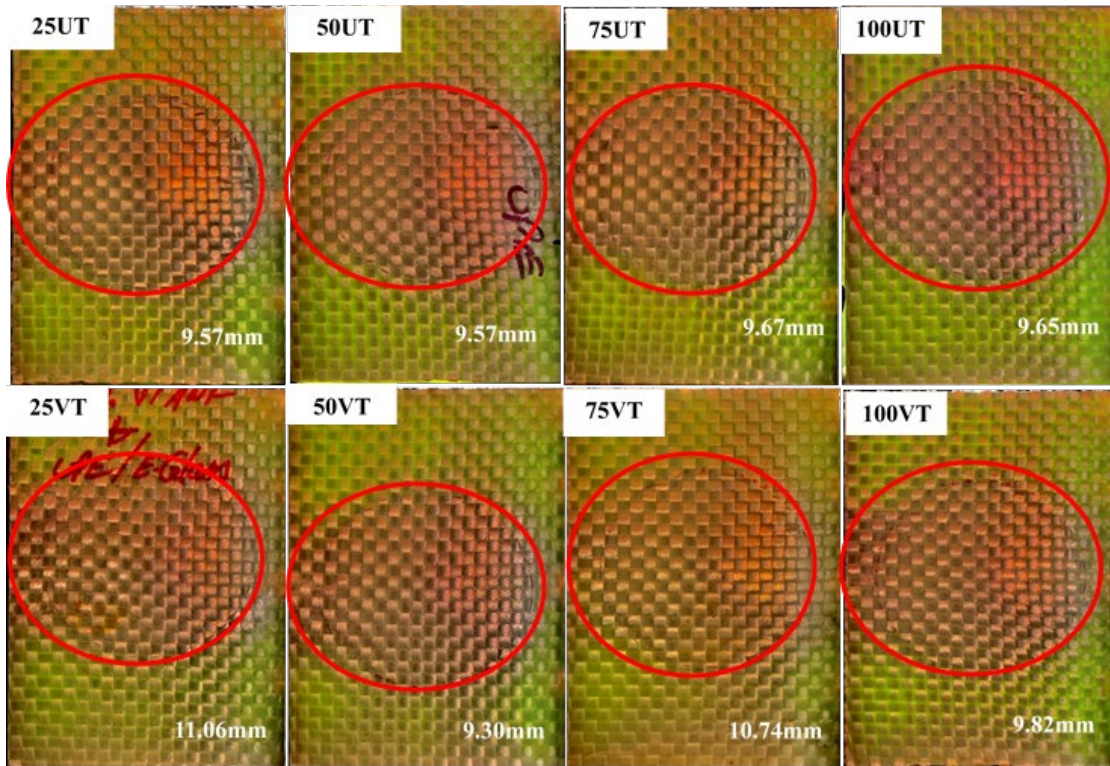


Figure 5.21: Back face cone formation and cone height representation in composites at impact energy level of 135J

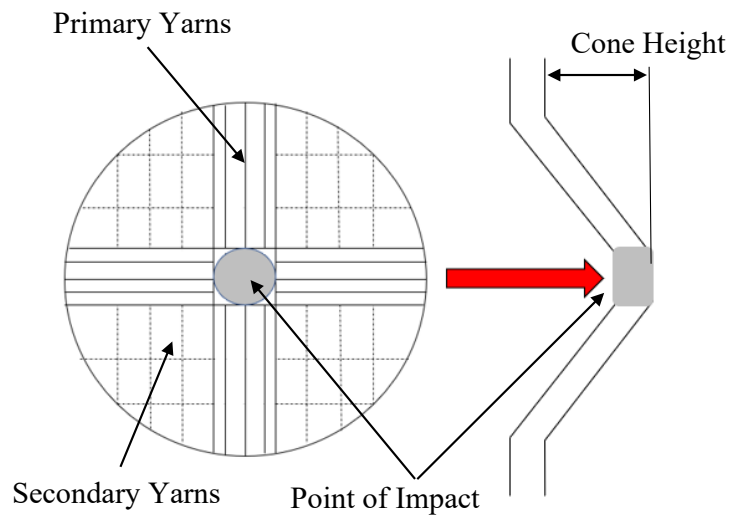


Figure 5.22: Illustration of cone formation and strain effect on primary, secondary yarns

Table 5.5 gives summary of displacement at peak loads and cone heights as observed from composites during damage absorption. The variation of damage in terms of displacement and cone height is illustrated in Figure 5.23. Higher displacement values

are a result of higher energy absorption indicating extended damage. The increased energy level resulted in increased displacement which is normal. The key differentiation is VT – Composite as compared to UT – Composite observed less displacement at peak load values, but the cone heights were almost similar. It was observed that more than 70% of the total displacement corresponded to cone height formation in samples. The inclusion of nanofillers into samples resists propagation of cracks by deflecting crack tips due to presence of dispersed alumina nanofibers. Matrix cracking, fiber matrix debonding and delamination are typically associated with matrix volume fraction and increase in matrix toughness by addition of nanofillers typically aids in higher energy absorption, higher peak loads and higher deflection in samples. At all energy levels as observed from values in table and graph, the crack deflection due to presence of alumina nanofibers resulted in higher displacements at peak loads and further increase in cone height formation.

Table 5.5: Summary of displacement at peak load, cone heights of UT and VT - Composite

	Displacement at Peak Load (mm)				Cone Height (mm)				Percentage of Cone height in displacement (%)			
	135J	170J	205J	240J	135J	170J	205J	240J	135J	170J	205J	240J
0	12.6	11.0	11.5	15.4	8.9	9.2	11.8	13.7	70.2	83.2	102.2	88.7
25UT	13.4	10.1	15.6	16.4	9.5	10.1	10.9	12.2	71.6	100.0	69.9	74.4
50UT	12.9	13.9	15.5	17.2	9.57	10.3	11.6	11.0	74.2	74.1	75.1	64.0
75UT	10.7	11.2	10.8	15.9	9.67	10.3	10.6	10.8	90.4	91.7	98.1	67.9
100UT	10.2	12.9	14.3	15.5	9.65	10.2	10.7	10.89	93.9	79.3	74.8	70.2
25VT	9.9	14.0	14.7	15.5	11.1	11.2	12.2	12.85	111.5	79.8	83.1	82.5
50VT	10.9	10.9	12.7	14.7	9.3	10.6	11.7	11.64	84.9	97.8	91.9	78.9
75VT	10.6	13.2	11.6	15.2	10.3	11.0	11.2	13.38	97.3	83.5	96.7	88.2
100VT	10.3	13.6	14.9	14.8	9.8	10.6	11.1	11.54	95.3	78.3	74.2	77.7

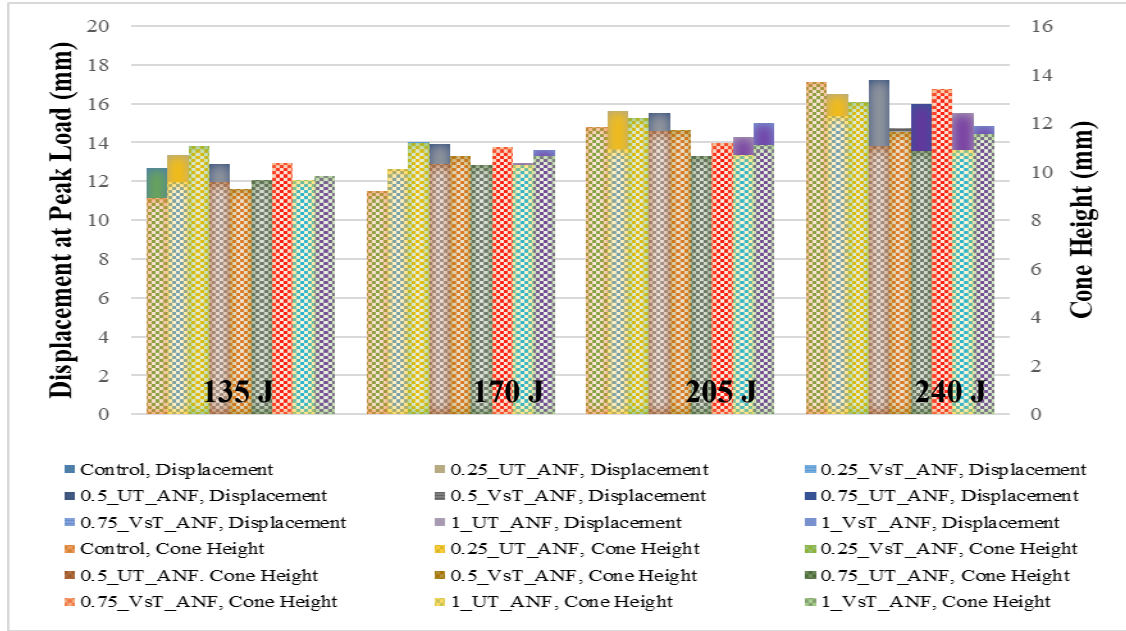


Figure 5.23: Displacement at peak load and cone height variation

5.5 Conclusions

The dynamic low velocity impact behavior of woven glass reinforced alumina nanofiber modified polyester composite laminates is studied and compared. Loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% for both UT - Composite and VT - Composite were studied for energy levels of 135J, 170J, 205J and 240J.

1. Fiber volume fraction, void fraction analysis revealed that increased loading levels resulted in increase of void content as well as fiber volume content. Surface treatment helped in reducing the void content because of the reduced viscosity even.
2. The energy absorption is significant as inferred from symmetry of impact load vs displacement curves. The symmetry of curve to peak load is an indication of energy absorption through inelasticity or damage but no penetration. The damage in composite is progressive and possibly matrix cracks as initiation points leading

to fiber matrix debonding and delamination as observed from the irregularities on ascending curve and no sudden drop in curve after reaching peak load.

3. Increase in energy levels increased manifested peak loads for 0.25wt%, 0.5wt% and 0.75wt% VsT_ANF_UPE/GPC composites as compared to other material systems. At 135J energy level, the peak load was enhanced by 14.5%, 13.12% and 17.52% for 25VT, 50VT and 75VT - Composite, respectively. At 170J energy level, peak load was not so significant. At 205J energy level, peak load was enhanced by 17.8%, 39.8% and 33.3% for 25VT, 50VT and 75VT - Composite, respectively. At 240J energy level, peak load was enhanced by -10.4%, 20.2% and 17.1% for 25VT, 50VT and 75VT - Composite, respectively. At higher energy levels, 0.5wt% and 0.75wt% loading levels with vinyl surface treatment is effective in manifesting maximum peak loads.
4. The stiffness calculation based on the slope of the elastic portion of the impact load vs displacement curve revealed that at lower energy levels the laminate stiffness response is low and at higher energy levels 50VT and 75VT - Composite manifested higher initial stiffness. The initial stiffness values represent the response of the laminate to induced energy. Higher stiffness values represent difficulty in crack propagation after impact before reaching peak load or maximum damage level. VT - Composite represented higher overall initial stiffness values indicating existence of crack pinning, crack restriction mechanisms during formation of matrix cracks.
5. The delamination threshold load which is defined as the first instance of estimated delamination which can be observed from the impact load vs impact duration plot,

increased with increase in peak load. From the impact load vs impact duration plots for all material systems, it was noteworthy to mention that 25VT, 50VT and 75VT - Composite observed DTL after reaching the peak load, indicating maximum energy absorption without reduction in residual strengths before attaining peak load. This observation is crucial in understanding the crack tip deflection by the efficiently dispersed alumina nanofibers restricting crack propagation to the interface of matrix and reinforcement.

6. The post impact damage analysis revealed no penetration of any of the composite laminates at all energy levels but cone formation on the side opposite of the impact. A comparison of displacement at peak load and cone height on the back face revealed that about 70% of the total displacement corresponds to the cone formation. A comparison of the cone height formation as a function of the loading content alone, at higher energy levels the cone height decreased indicating change in energy absorption mode from cone height to internal fiber matrix debonding and delamination.

6. GLASS FIBER REINFORCED ALUMINA NANOFIBER FILLED POLYESTER COMPOSITES: BALLISTIC IMPACT CHARACTERIZATION

Composite materials due to their high stiffness to weight ratios, have become primary choices in major f the industries. One of the major industries which can take advantage of composite materials is the ballistic resistant material industry. Laminated composite materials owing to their light weight and tailorable properties can be used for light weight ballistic resistant structures, medium tactical vehicles, safe rooms, tornado shelters, underground storage tanks to name a few. The composite materials can be promising candidates imparting mobility, high protection without compromising the residual properties. In case of ballistic impact, the induced velocity or energy is due to a propelling projectile often having relatively low mass and speeds of projectile approaching 1000m/s. As explained in chapter 1, the contact times of projectile and target is very short, does not giving the material enough time to respond thus restricting the response to location of impact (Vaidya, 2011).

During a ballistic event, the kinetic energy of the projectile is absorbed through synergistic events of cone formation, secondary and primary yarn deformation, tensile failure, delamination and matrix cracking (Naik et al., 2006). Amongst the events occurring during projectile inhibition in the composite, cone formation, tensile failure, yarn deformation corresponds to the suitable selection of fabric. Matrix selection is crucial since it enables efficient load transfer between fiber bundles and delamination which is a major damage mechanism is influenced by initiation and propagation of matrix cracks to the interface of fiber and matrix.

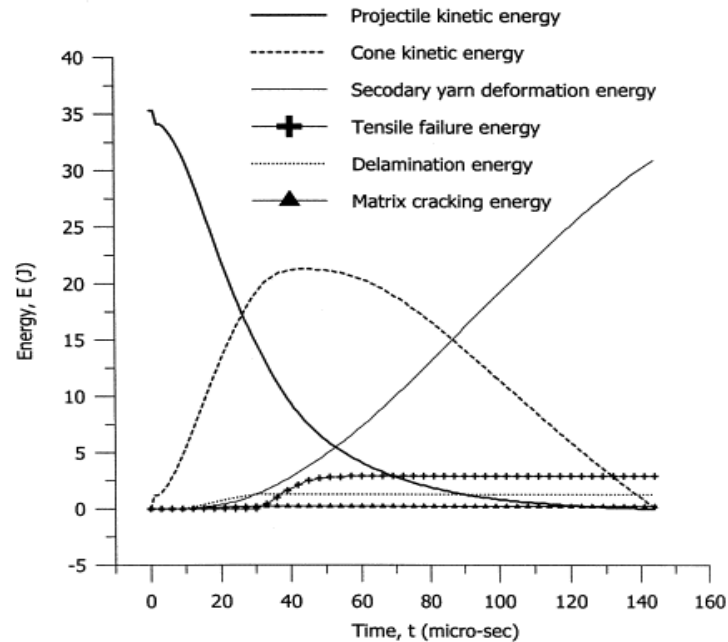


Figure 6.1: Energy absorption mechanisms during a ballistic impact event (Naik et al., 2006)

Amongst the ballistic fibers listed in chapter 1, aramid fibers (trade name: Kevlar), carbon fibers, glass fibers, UHMWPE fibers are extensively tested against ballistic impact. Kevlar fibers reinforced polymer (KFRP) composites are extensively used for body armor applications. Carbon fibers are one of the primary candidates in the aerospace, aircraft industry. Since these structures are continuously under threat from runway debris, bird strikes, and foreign object impacts much research has been concentrated with respect to carbon fiber as reinforcement. However, carbon fiber reinforced polymer (CFRP) composites exhibit a brittle behavior and does not provide excellent impact resistance (Davies & Zhang, 1995). UHMWPE are one class of ballistic resistant fibers which offer better impact resistance, but the fact that their compressive properties are poor make them less ideal choice when residual strengths are critical to maintain structural integrity after impact. As provided in table 1.4, carbon fiber, kevlar fiber and UHMWPE fiber are expensive materials which makes them suitable for exotic

applications. It is widely accepted from the cost point of view that glass fibers offer affordability with excellent combination of ductility, toughness and strength (Brosius, 2016b) which makes it a suitable choice for developing affordable ballistic resistant structures.

In terms of type of reinforcement, architecture of fabric and thickness, some selected literature was presented here. Mines et al. conducted high velocity perforation studies on 6ply, 12ply and 24ply composite laminates with E-glass as the reinforcement and polyester as the resin which were fabricated using wet layup and cold curing. It was noted that thickness had an influence on the damage absorption behavior of composite laminates, where in delamination becomes a major energy absorption mechanism. In terms of architecture, it was noted that there is no difference in the behavior of laminates comprising woven roving or stitched. From the studies, it was noted that glass polyester composites have greater strain sensitivity, which would enhance the dynamic enhancement factors as compared to CFRP and KRP contributing to higher perforation energies (Mines, Roach, & Jones, 1999). Kim et al. studied delamination failure of woven fabric composites and noted that woven fabric composites show 4-5 times higher GIC values because of the presence of undulations which aid in large fracture areas and multiple crack fronts. It was noted that woven fabric laminates exhibit lower maximum load, high ductility index and high residual properties (Kim & Sham, 2000). Hosur et al. investigated the effect of stitching on the ballistic impact behavior of plain and satin weave fabric laminates. It was noted that for thin samples the style of weave does not have a major role to play in ballistic limit enhancement. However, ballistic energy increase was profound for satin weave architecture as compared to plain weave and the

increase was about 13%. Woven architecture showed 37% higher ballistic limit when compared to stitched composite laminates, indicating stitching is not that effective for ballistic applications. This is because the projectile will penetrate the stitched laminates at much lower incident velocities in comparison with unstitched reducing ballistic limit (Hosur et al., 2004).

Matrix in the form of polymer has a significant effect on composite properties in terms of efficient stress transfer. However, most of thermoset polymer matrices used along with reinforcements are brittle in nature due to their high crosslinking. One key approach in view of increasing the toughness of matrix is to incorporate nanomaterials at suitable loading levels to achieve enhanced ballistic resistance. As per authors knowledge, a very limited research has been done on increasing the ballistic impact resistance of E-glass polymer composites by incorporating nanofillers, some of which is presented below. Nanoclay is studied for its effectiveness in polyester resin to enhance ballistic performance of respective composites. Esfahani et al. studied 1.5wt% and 3wt% loading levels of nanoclay dispersed in polyester resin. The group noted that inclusion of nanoclay at 1.5wt% in polyester resin resulted in enhanced ballistic performance of respective composites in terms of reduced residual velocities (Esfahani, Esfandeh, et al., 2012). Pol et al. in their study of assessing the influence of nanoclay on ballistic behavior of E-glass/epoxy laminates considered impact velocities of 130, 142 and 155m/s by a flat end projectile. Loading levels of nanoclay in epoxy were 1,2,3,5 and 7wt%. It was observed that nanoclay inclusion had a significant effect on residual velocities for 130m/s and 142m/s incident velocities. The residual velocities were less for 5wt% nanoclay infused composites with enhanced damage area indicating good energy absorption (M. H.

Pol, Liaghat, & Hajiarazi, 2013). Rahman et al. used amino functionalized MWCNTs to enhance the ballistic performance of E-glass/epoxy composites. It was reported that 0.3wt% loading level increased the ballistic limit velocity by 6% and further addition of MWCNT did not show any increase. The major observation made was in terms of damage tolerance, where nanomodified composites exhibited less damage size. The addition of nanofillers proved to increase the fracture toughness which is an effect of increased interfacial strength (M. Rahman et al., 2013).

Woven glass fiber polyester composites owing to their ductile nature, when compared to brittle epoxy-based composites offer good impact resistance. In this study, impact strength of fourteen-layer 0/90 woven E-glass fabric reinforced polyester composites modified with alumina nanofibers are studied. One set of composites were modified with untreated alumina nanofibers and second set were modified with vinyl silane coupling (organic content 6-7%) agent treated alumina nanofibers. For a uniform distribution in polymer matrix, better wettability and interaction, surface energy of fiber should be close to surface energy of polymer. Loading levels of 0.25wt%, 0.5wt%, 0.75wt% and 1wt% were used for both sets of composites laminates. The glass polyester composites modified with untreated alumina nanofibers are here from referred to as UT-Composite and composites modified with vinyl silane treated alumina nanofibers as VT-Composite. Benzoyl Peroxide acquired from Sigma-Aldrich is used as curing agent with heat as external simulator.

6.1 Characterization

6.1.1 Ballistic impact setup

Ballistic testing on composite laminates prepared in-house are tested at a controlled facility of Waco Composites in Waco, TX. The test setup used was according to National Institute of Justice (NIJ) standard ("Ballistic Resistant Protective Materials - NIJ Standard 0108.01," 1985) which consists of a single stage gun to propel projectile through a 10 in barrel. Longer barrel was used in this study to get consistent velocities of projectile. Before testing, the barrel was ensured to be smooth to prevent any friction with projectile which could alter velocities. The distance between gun and laminate is maintained at 6096 mm (20ft) and witness plate was placed at 482.6 mm on opposite side of composite. Two chronographs are used to record velocities of projectile and are placed at 53.89 mm and 2971.8mm from composite, respectively. The velocities as recorded by both the chronographs recorded consistent velocities with negligible deviation in velocities. Schematic of NIJ test setup is provided in Figure 6.2.

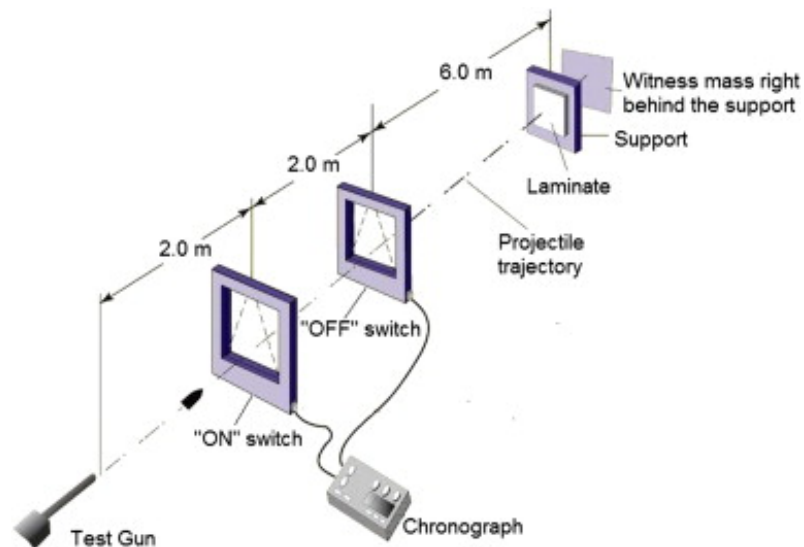


Figure 6.2: Schematic of test setup according to NIJ standard ("Ballistic Resistant Protective Materials - NIJ Standard 0108.01," 1985)

The composite samples of dimensions 152.4mm x 152.4mm were placed against support frame and are clamped on four sides to prevent movement. Since the fixture can accommodate only 12in x 12in samples, two composite fixtures of 12in x 12in with 4 in square cut and 4in diameter cut are placed on either side of sample so that there is no variation in boundary conditions. The actual test up of Waco Composites for ballistic testing is shown in Figure 6.3 and projectile, composite laminate details are provided in Table 6.1. It was ensured that all projectile impacts take place in center of the composite sample. In this study, damage on witness plate was taken as a measurement of identifying pass or fail of composite sample against the chosen velocity. There was no provision of calculating residual velocities, hence energy absorbed is calculated only for samples which confined projectile. The composite samples were tested against 9mm, 124 grain, Full Metal Jacket (FMJ) lead core bullets, a standard at varying velocities according to Underwriters Laboratory (UL) 752 (laboratory, 2005) Level 1 and Level 6 standards. The UL Level 1 specifies a material to endure 358m/s velocity and UL level 6 specifies a maximum velocity of 469m/s for the material to withstand. The tests in this study indicate if the material qualifies based on visual perforations if any observed-on witness plate behind the target post testing. The configuration, properties of composites produced for investigation are provided in Table 6.1. The consistency in thickness, density and fiber volume fraction was noted, which indicates fine-tuned manufacturing process. The void fraction increased with addition of alumina nanofiber content; however, values of void fraction were lesser when alumina nanofibers were surface treated.



Figure 6.3: Test setup used for ballistic testing in Waco composites facility

Table 6.1: UT and VT - Composite sample data for ballistic testing.

Sample	Thickness mm	Density g/cm ³	Constituent volume fraction		
			(%)		
			V _f	V _m	V _o
Composite	7.25	1.98	57.9	40.0	2.1
25UT – Composite	7.3	2.00	63.5	30.5	6.0
50UT - Composite	7.35	1.98	62.5	30.7	6.8
75UT – Composite	7.32	2.02	67.2	24.8	8.0
100UT – Composite	7.36	2.00	66.8	23.6	9.5
25VT – Composite	7.35	2.01	61.9	34.4	3.6
50VT – Composite	7.34	2.02	64.3	30.8	4.9
75VT – Composite	7.4	2.01	66.6	27.2	6.2
100VT - Composite	7.36	2.00	66.1	25.1	8.8

6.2 Results and discussion

The samples were tested for their efficiency to defeat maximum projectile velocities of UL level 1 and level 6. For velocities of projectile which were contained by alumina nanofiber modified polyester glass composites, absorbed energy was calculated by using kinetic energy equation.

$$\text{Absorbed Energy} = E_a = \frac{1}{2}mv^2 - \frac{1}{2}mu^2 \quad (1)$$

Where m, v and u are mass of projectile (0.00803 KG), incident velocity and residual velocity.

In present study, there was no provision to calculate residual velocity of projectile, hence absorbed energy values were reported only for samples and velocities which suppressed projectile. Absorbed energy is a main parameter to assess and evaluate damage process in a composite laminate and equation 1 is used to calculate absorbed energy. A fully instrumented set up gives information on incident velocities, residual velocities which can be utilized to calculate degree of damage in composite. In a ballistic impact scenario, incident impact energy is usually kinetic energy of projectile and if no penetration occurs all the energy is dissipated in composite. Energy absorption in impact event essentially occurs due to interaction of projectile with composite sample via different mechanisms and these mechanisms widely differ as compared to low velocity impact. This is because of projectile geometry and higher velocities which change globalized damage to localized damage. The velocities at which composite samples were tested, absorbed energy values and remarks are presented in Table 6.2. The maximum velocity which was impeded by respective samples and minimum velocity at which there was penetration is represented in Table 6.3 and is represented in Figure 6.4. From the data it is evident that alumina nanofiber contributed to higher impeded velocities thus higher absorbed energy values. 0.25wt%, 0.5wt% and 0.75wt% loading levels has seen an increase peak embedded velocity values and absorbed energy. The effect of surface treatment of alumina nanofibers did not show any positive effect on impeding velocities and there was no significant change observed. The composite laminates in all categories were tested for their capability to reach level 1 initially and further for capability to reach level 6. All composite samples sustained level 1 energy velocities and nanomodified composites showed an enhancement in impeding velocity in range of 15%-19%.25UT,

50UT and 75UT – Composites have enhanced defeating velocity by 19.28%, 18.82% and 19.75% respectively when tested against level 1 max velocity of 394 m/s. The 25VT, 50VT and 75VT – Composites showed similar enhancement in defeating velocity with values of 19.21%, 18.28% and 18.90% respectively when tested against level 1 max velocity of 394m/s. Any change in boundary conditions does not seem to affect the energy absorption behavior but however there is influence on the initial mode of failure suggesting the response of material for a given energy. Since all dimensions, boundary conditions, sample dimensions remain same any change in energy absorption or material behavior under ballistic impact loading can be identified by damage modes. It is almost impossible to generate an understanding from static loading and low velocity impact loading as damage mechanisms generated are dependent on strain sensitivity of material. In case of static loading and low velocity impact loading, strain rates are very small resulting in globalized damage response of material. In case of ballistic impact loading, strain rates are higher which does not give the material enough time to respond to the induced loads resulting in localized damage (Domun et al., 2019).

Table 6.2: Ballistic impact results for UT and VT – Composite

Sample	Specimen No.	Velocities	Remarks	Absorbed Energy
		mps		J
Composite	1	433.71	Embedded	755.24
	2	464.8	Embedded	867.40
	3	465.41	Embedded	869.67
	4	465.71	Embedded	870.80
	5	470.89	Penetrated	-
	6	472.11	Penetrated	-
	7	476.99	Penetrated	-
	8	477.9	Penetrated	-
25UT – Composite	1	427.92	Embedded	735.21
	2	432.19	Embedded	749.95
	3	465.71	Embedded	870.80
	4	469.98	Embedded	886.84
	5	472.42	Penetrated	-
	6	476.07	Penetrated	-

	7	489.79	Penetrated	-
50UT - Composite	1	419.38	Embedded	706.16
	2	467.24	Embedded	876.53
	3	468.15	Embedded	879.95
	4	471.81	Penetrated	-
	5	475.77	Penetrated	-
	6	476.38	Penetrated	-
	7	488.88	Penetrated	-
	8	499.54	Penetrated	-
75UT – Composite	1	424.57	Embedded	723.74
	2	457.79	Embedded	841.43
	3	463.58	Embedded	862.85
	4	471.81	Embedded	893.76
	5	484.61	Penetrated	-
	6	487.05	Penetrated	-
100UT – Composite	1	455.96	Embedded	834.72
	2	469.98	Penetrated	-
	3	473.33	Penetrated	-
	4	482.47	Penetrated	-
25VT – Composite	1	435.84	Embedded	762.68
	2	468.76	Embedded	882.24
	3	469.06	Embedded	883.37
	4	475.77	Penetrated	-
	5	476.07	Penetrated	-
	6	477.9	Penetrated	-
	7	479.12	Penetrated	-
	8	482.17	Penetrated	-
50VT – Composite	1	419.08	Embedded	705.15
	2	430.97	Embedded	745.73
	3	448.03	Embedded	805.93
	4	465.41	Embedded	869.67
	5	466.02	Embedded	871.96
	6	471.5	Penetrated	-
	7	480.34	Penetrated	-
	8	485.83	Penetrated	-
75VT – Composite	1	420.3	Embedded	709.26
	2	433.71	Embedded	755.24
	3	467.85	Embedded	878.82
	4	468.45	Embedded	881.07
	5	470.59	Penetrated	-
	6	474.86	Penetrated	-
	7	480.04	Penetrated	-
	8	485.22	Penetrated	-
100VT – Composite	1	436.45	Embedded	764.81
	2	459.31	Penetrated	-
	3	464.8	Penetrated	-
	4	487.96	Penetrated	-

Table 6.3: Summary of impeded and penetration velocities of UT and VT – Composites

Sample	Maximum Impeded Velocity	Maximum Absorbed Energy	Minimum Penetration Velocity	L-1 Max.	L-6 Max.
Composite	465.71	870.8	470.89	Pass	Fail
25UT – Composite	469.98	886.8	472.42	Pass	Pass
50UT – Composite	468.15	879.9	471.81	Pass	Fail
75UT – Composite	471.81	893.8	484.61	Pass	Pass
100UT – Composite	455.96	834.7	469.98	Pass	Fail
25VT – Composite	469.67	885.7	475.77	Pass	Pass
50VT – Composite	466.02	872.0	471.50	Pass	Fail
75VT – Composite	468.45	881.1	470.59	Pass	Fail
100VT – Composite	436.45	764.8	459.31	Pass	Fail

As observed in Figure 6.4, there is no significant change in the impeding velocities beyond 5m/s. The formulations at 0.25wt%, 0.5wt% and 0.75wt% showed similar improvement regardless of surface treatment of ANF. An understanding on damage failures, as represented in Figure 6.12 to 6.18, can give us an perceptiveness into post damage behavior of composite laminates.

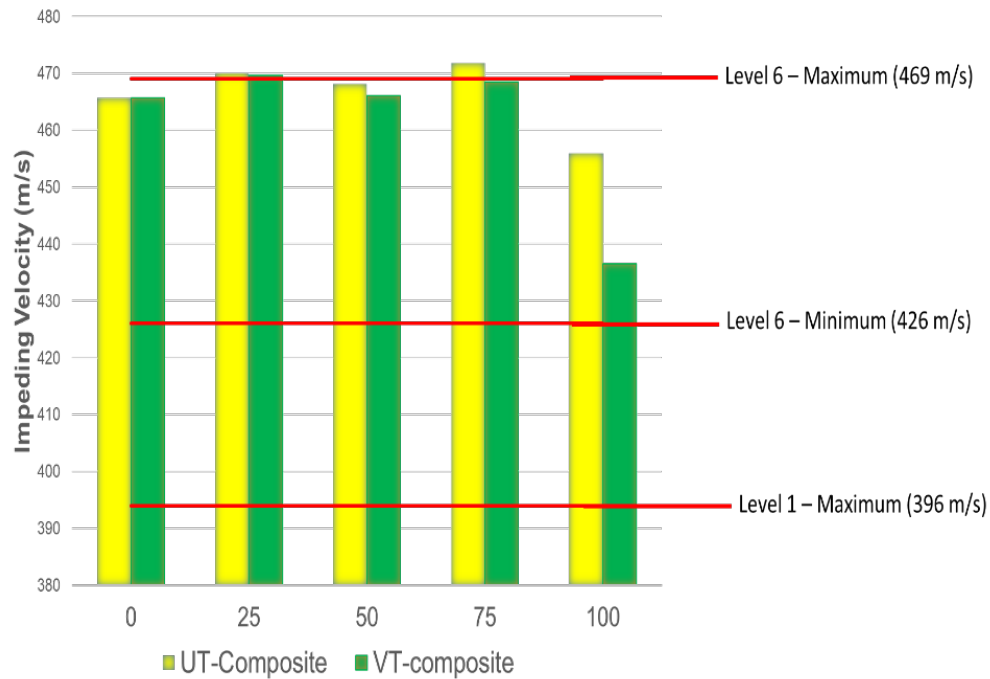


Figure 6.4: Variation in impeded velocities for UT and VT – Composites.

Table 6.4 Configuration and the physical properties of UT and VT - Composites

Sample	Density	Thickness	Areal Density	Impeding Velocity	Energy Absorbed	Normalized Energy
	g/cm ³	mm	g/cm ²	m/s	J	J/mm
Commercial (Level-6)		9.50		469.00	883.14	92.96
Composite	1.98	7.25	1.44	465.71	870.80	120.11
25UT - Composite	2.00	7.30	1.46	469.05	896.07	122.75
50UT - Composite	1.98	7.35	1.46	468.15	879.95	119.72
75UT - Composite	2.02	7.39	1.49	471.81	893.76	120.94
100UT - Composite	2.00	7.35	1.47	455.96	834.72	113.57
25VT - Composite	2.01	7.35	1.48	469.06	883.37	120.19
50VT - Composite	2.02	7.39	1.49	466.02	871.96	117.99
75VT - Composite	2.04	7.30	1.49	468.45	881.07	120.69
100VT - Composite	2.00	7.35	1.47	436.45	764.81	104.06

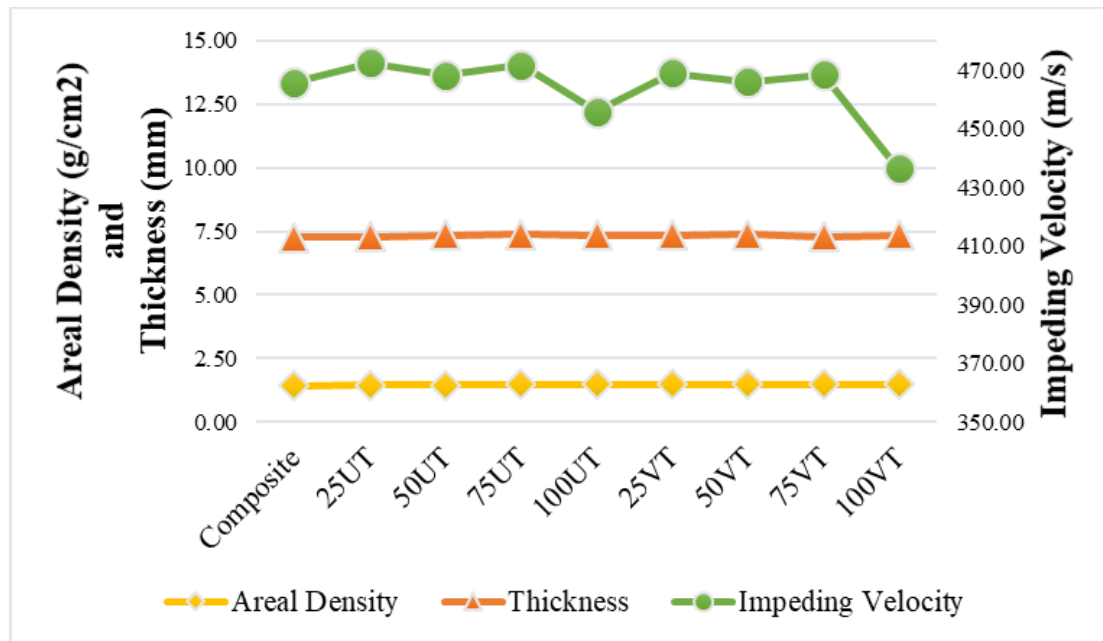


Figure 6.5: Relationship between areal density, thickness and impeding velocity of UT and VT - Composite

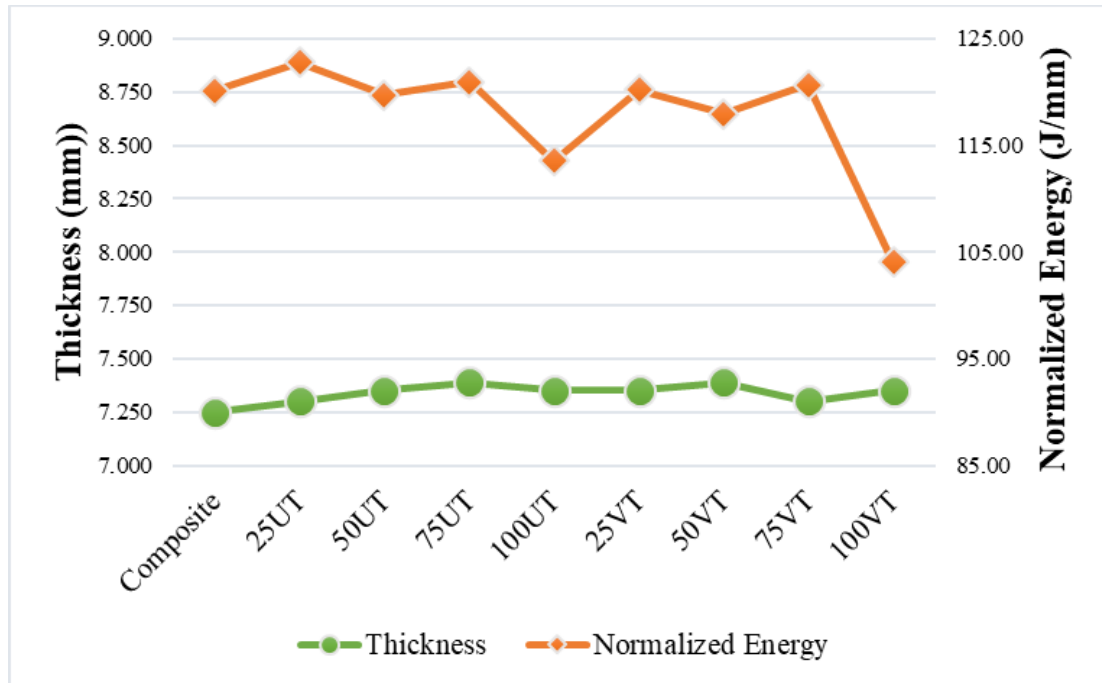


Figure 6.6: Relationship between thickness and normalized energy of UT and VT – Composite

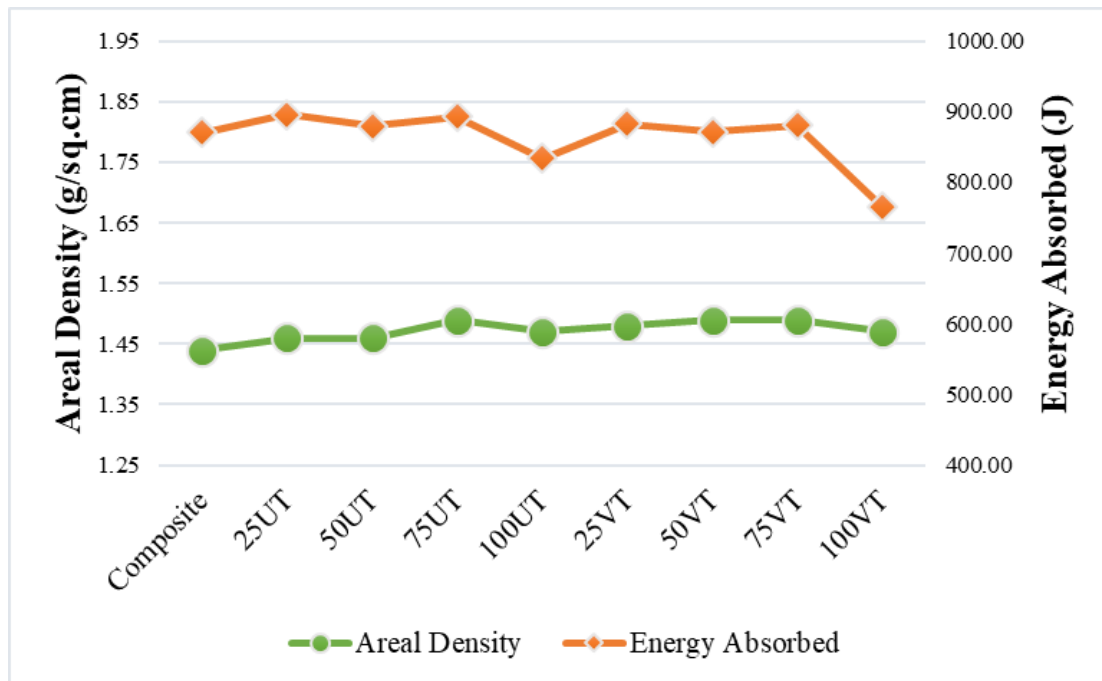


Figure 6.7: Relationship between areal density and energy absorbed of UT and VT – Composite

Table 6.4 gives weight, thickness, areal density and properties of composites which survived velocity in each category of developed composites. The areal density was

calculated by multiplying the average density with average thickness. The normalized energy is calculated by dividing energy absorbed by thickness of sample tested. Figure 6.5, Figure 6.6 and Figure 6.7 gives the illustration of impeding velocity, normalized energy and energy absorbed variation as a function of areal density and thickness for the composites. In general, increase in areal density would enhance ballistic velocity and ballistic limit of the composite, as the bullet has to overcome the closely packed fabric in order to perforate. In our case, areal density, thickness did not vary significantly. The variation in energy absorbed and impeding velocity is purely dependent on alumina nanofiber loading content in our study.

6.3 Post damage evaluation

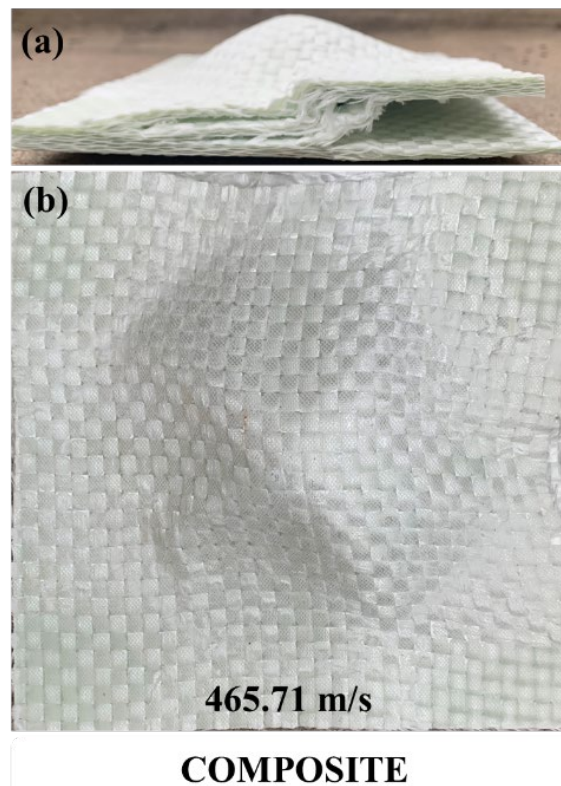


Figure 6.8: (a) Side view and (b) back face damage showing cone formation for composite

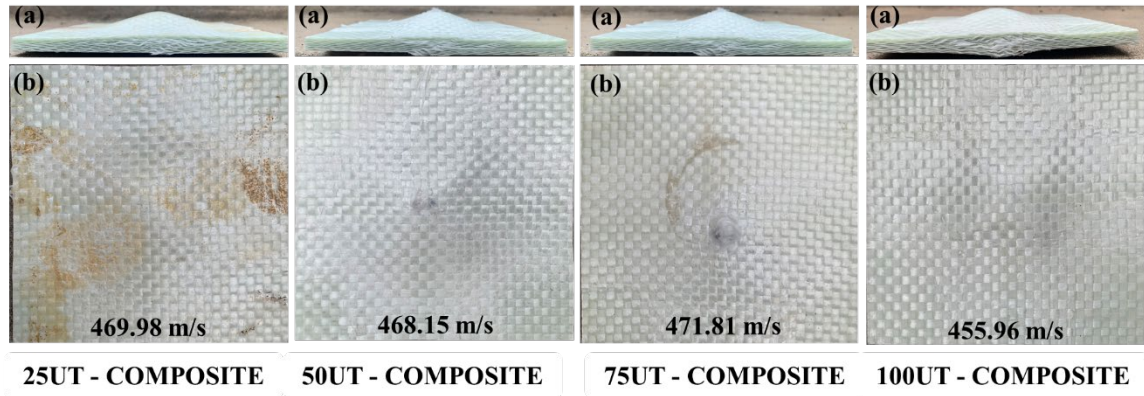


Figure 6.9: (a) Side view and (b) back face damage showing cone formation for 25UT, 50UT, 75UT and 100UT composite

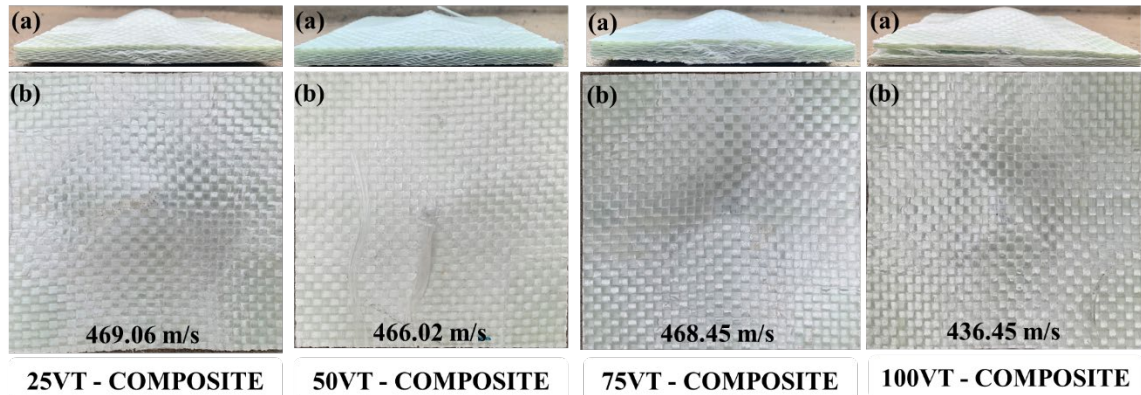


Figure 6.10: (a) Side view and (b) back face damage showing cone formation for 25VT, 50VT, 75VT and 100VT composite

As discussed earlier in the chapter, projectile energy is mainly absorbed due to cone formation. Figure 6.8, Figure 6.9 and Figure 6.10 give an illustration of back face cone formation during projectile energy absorption. Side view of impacted specimens are provided in same figures, but not much information can be deduced from these figures. The details on impeding velocity, areal density and cone height are presented in Table 6.5. The cone heights represented here are for the composites which survived maximum impeding velocities. Cone heights for samples which observed penetration are recorded using the image J software and it was noted that cone heights were less in penetrated samples. When a projectile encounters the target, both systems exchange kinetic energy

and pressure. In case of deformable projectile, if pressure exerted by composite is higher projectile deforms and is held inside the composite. During this phase, the projectile needs to compress the material in front of it and push away fibers in its path. If the pressure exerted by projectile is higher, projectile overcomes forces offered by composite and penetrates without giving composite enough time to react.

Table 6.5: Cone height variation for composites at maximum impeding velocities.

Sample	Thickness	Areal Density	Impeding Velocity	Energy Absorbed	Cone Height
	mm	g/cm ²	m/s	J	mm
Composite	7.25	1.44	465.71	870.80	24.85
25UT - Composite	7.30	1.46	472.42	896.07	17.28
50UT - Composite	7.35	1.46	468.15	879.95	22.01
75UT - Composite	7.39	1.49	471.81	893.76	25.51
100UT - Composite	7.35	1.47	455.96	834.72	19.66
25VT - Composite	7.35	1.48	469.06	883.37	19.64
50VT - Composite	7.39	1.49	466.02	871.96	20.98
75VT - Composite	7.30	1.49	468.45	881.07	18.62
100VT - Composite	7.35	1.47	436.45	764.81	17.56

The damage profile of the composite laminates under ballistic impact varies depending on the thickness of composite. For varying thicknesses, damage profile as studied by Gillert et al is represented in Figure 6.11. The damage in glass reinforced composite laminates is manifested as delamination of layers of fabric, shearing of fibers in path of projectile, fragmentation of projectile causing matrix cracking and fiber breakage and perforation of composite laminate. In thin laminates, damage spreads through the thickness and increases in size as projectile exits laminate, whereas in case of thick laminates the damage spread is observed in shape of an hour glass (Gellert, Cimpoeru, & Woodward, 2000). This phenomenon is explained due to the radial pressure created by the compression of material ahead of projectile, causing an upthrust. If the incident energy is greater than energy required for delamination, layers delaminate easily

causing “dishing” and final exit of the projectile. If the layers easily deform in the direction of projectile path, then this “dishing” prevents the perforation of projectile.

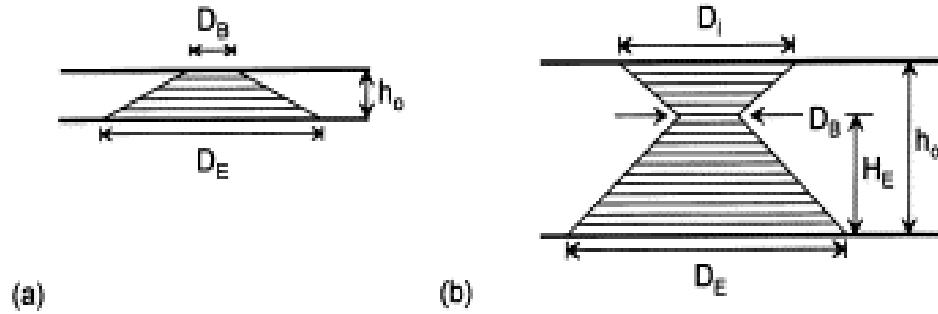


Figure 6.11: Damage profile as observed in (a) thin composites and (b) thick composites under ballistic impact loading (Gellert et al., 2000)

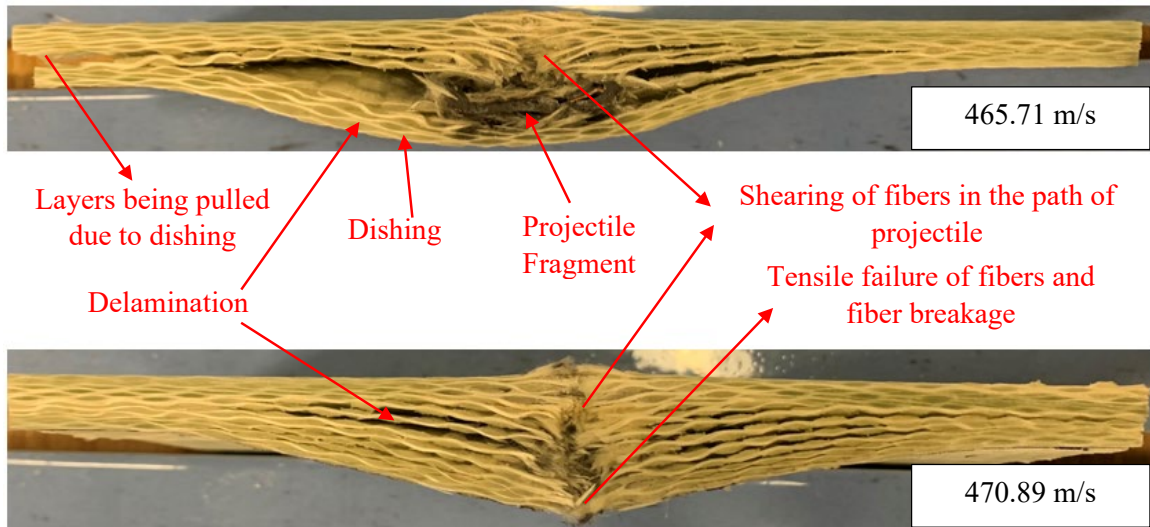


Figure 6.12: Damage profile as observed in Composite at (a) maximum impacting velocity of 465.71 m/s and (b) minimum penetration velocity of 470.89 m/s

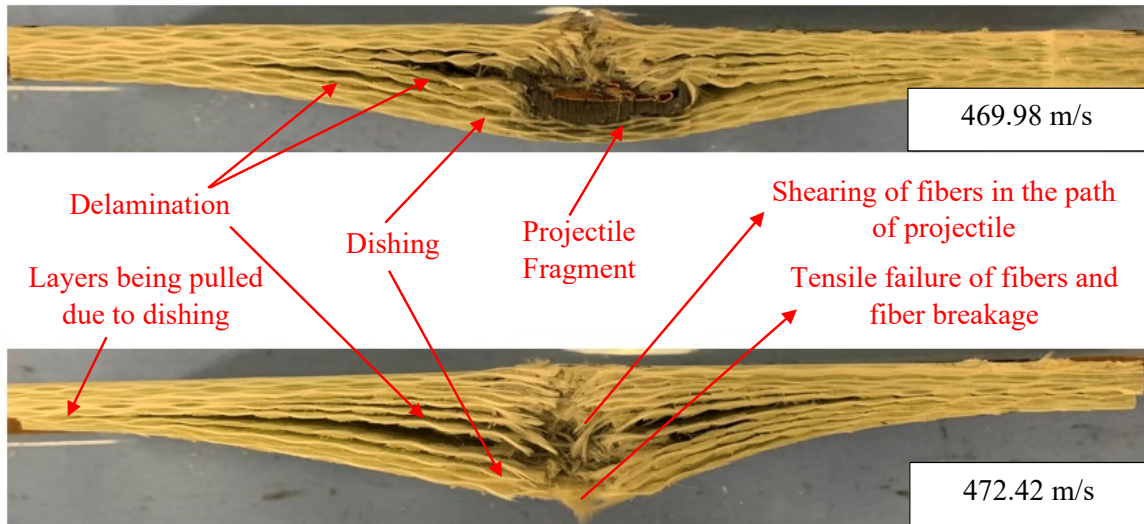


Figure 6.13: Damage profile as observed in 25UT - Composite at (a) maximum impeding velocity of 469.98 m/s and (b) minimum penetration velocity of 472.42 m/s

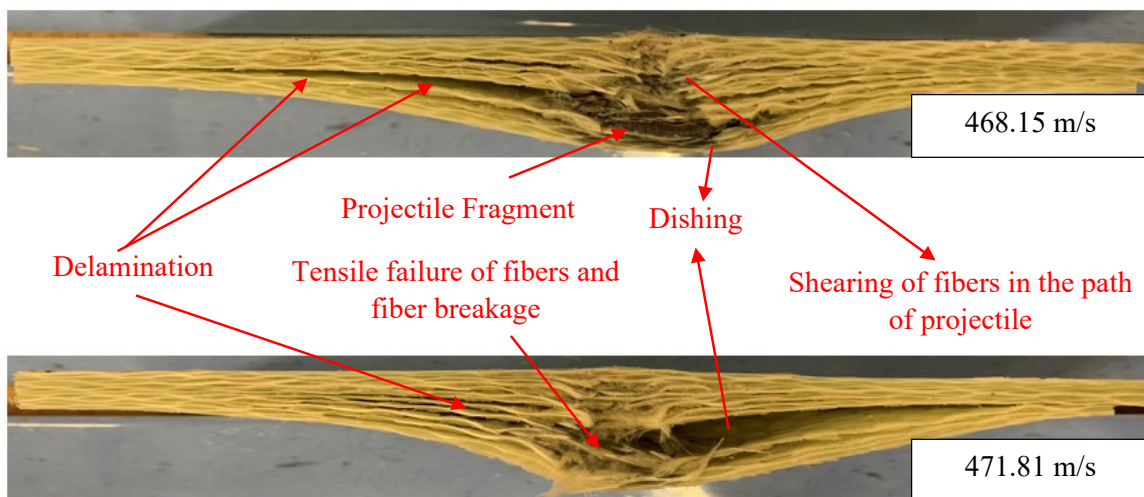


Figure 6.14: Damage profile as observed in 50UT - Composite at (a) maximum impeding velocity of 468.15 m/s and (b) minimum penetration velocity of 471.81 m/s

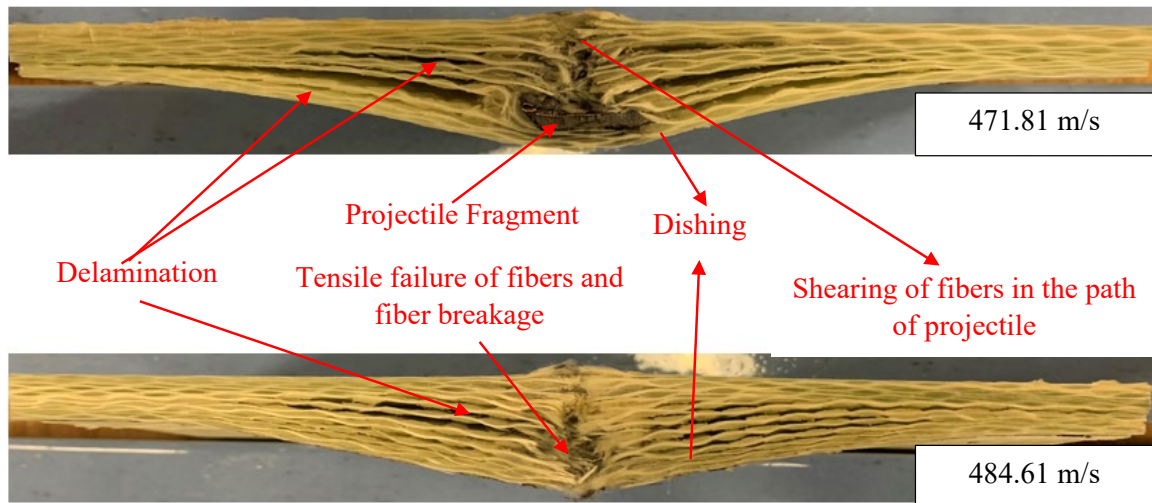


Figure 6.15: Damage profile as observed in 75UT - Composite at (a) maximum impeding velocity of 471.81 m/s and (b) minimum penetration velocity of 484.61 m/s

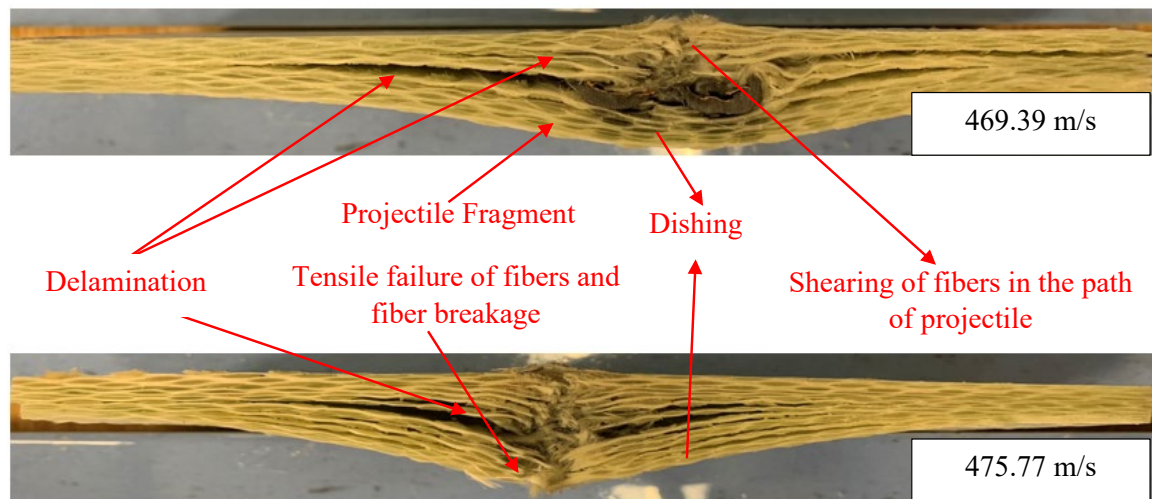


Figure 6.16: Damage profile as observed in 25VT - Composite at (a) maximum impeding velocity of 469.39 m/s and (b) minimum penetration velocity of 475.77 m/s

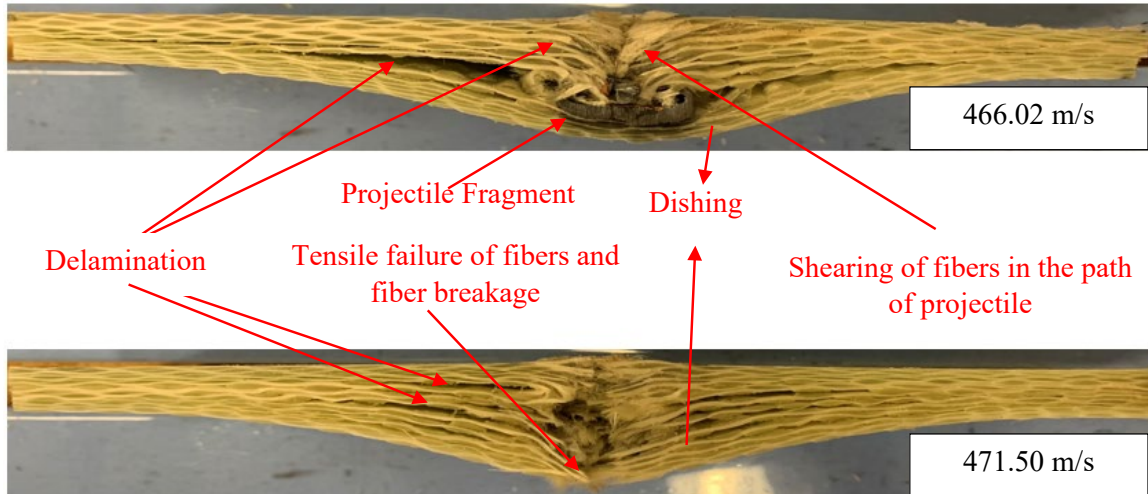


Figure 6.17: Damage profile as observed in 50VT - Composite at (a) maximum impacting velocity of 466.02 m/s and (b) minimum penetration velocity of 471.50 m/s

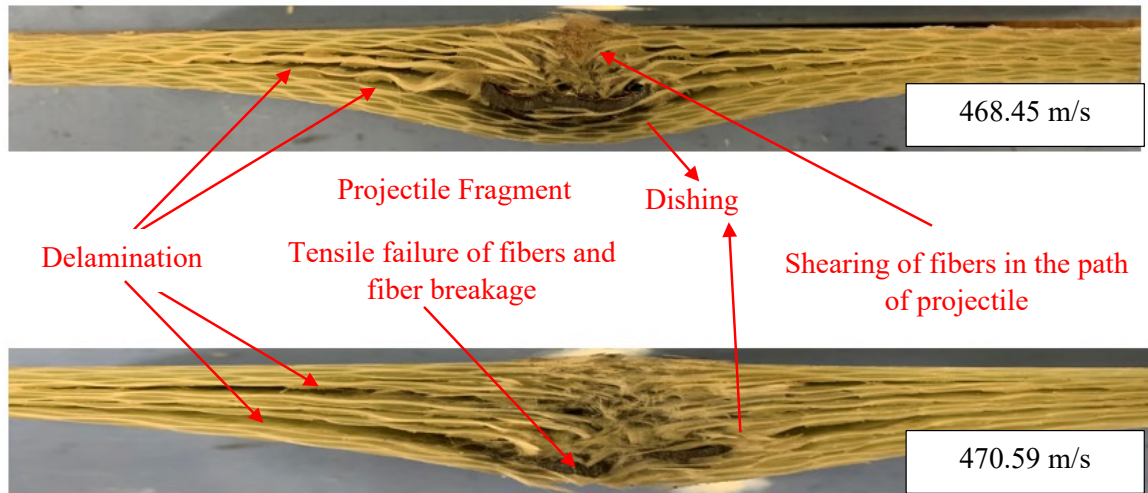


Figure 6.18: Damage profile as observed in 75VT - Composite at (a) maximum impacting velocity of 468.45 m/s and (b) minimum penetration velocity of 470.59 m/s

The sample was sectioned along the path of projectile to observe failure inside the damage. As observed from Figure 6.12 to Figure 6.18, main mode of damage/energy absorption is through delamination. At the interface where projectile is contained in composite, delamination is largest than where projectile penetrates. Matrix cracking and delamination absorb part of kinetic energy of projectile. The matrix cracks grow until interfacial region and creates fiber matrix debonding resulting in delamination. The increase in volume of matrix cracks reduce interlaminar strength of composite. When

projectile is contained in composite at end of ballistic event, a few delaminated areas are left and bend rather than delaminate enhancing cone formation (Naik & Doshi, 2008). The yarns directly below projectile are in direct tension and until yarns reach strain energy required to failure, they contribute towards cone formation thus enhancing energy absorption. If incident impact energy exceeds energy absorption limit of composite laminate, the projectile penetrates, and damage is more localized and is lower than full penetration (M. Rahman et al., 2013; Vaidya, 2011). In case of control composites, the delamination on top layers through middle layers are observed. The delamination in middle layer when projectile is arrested is extensive for control composites. The 25UT, 50UT and 75UT – Composite which withstood impeding velocities of 465.71 m/s, 469.98 m/s and 468.15 m/s has seen delamination was extensive in top layers and dishing phenomenon was observed in containing projectile. However, in VT – Composite, delamination was larger when the projectile is arrested, but it was observed that top layer delamination as observed in UT - Composite. Thus, delamination resistance was somewhat reduced as observed for VT - Composite. It was observed in all cases that pressure wave starting from the impact point directed along yarns continuing to edge of composite. The yarns do not fail during initial stress rise when projectile velocity is below ballistic limit and therefore promotes higher energy absorption of the laminate. The shear failure of plies continues until projectile is arrested by providing enough resistance through dishing. If velocity of projectile increase beyond ballistic limit, yarns of fabric do not have sufficient time to respond to transverse deflection causing failure of yarns by pushing aside and slipping past the rest of yarns (Ali et al., 2019). Except for fiber splitting, shear failure and tensile failure of the yarns during perforation there was

no shear plugging observed for composite. In a ballistic impact scenario, where damage is more localized fiber shear failure or fiber breakage is typically observed only at point of impact, but propagation of wave resulted in delamination (Abrate, 1991). The ductile nature of woven glass fiber reinforced polyester composites results in more flexible composite laminates thus enhancing energy absorption though easy deformation. The failure zones associated with ballistic impact response of composite laminates is illustrated in Figure 6.19 and is understood to be composed of shear failure of fibers in the path of projectiles followed by tensile failure of fibers and then delamination as main damage mode.

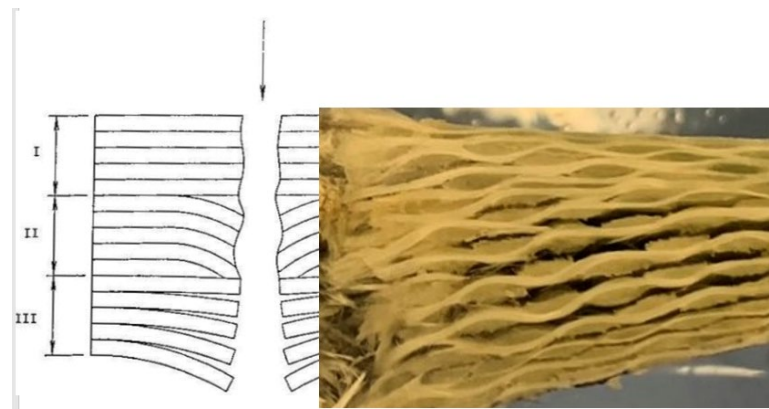


Figure 6.19: Failure modes and zones during ballistic impact perforation (Abrate, 1991).

The failure modes representing Figure 6.19 can be observed in all composite laminates tested in this present research study. The initial high failure strain of fabric in conjunction with matrix resulted in energy absorption of propelling projectile and when the energy is greater than failure strain of constituents there was penetration. However, in our study the static properties on neat polyester coupons and glass fiber reinforced polyester composites did not show any relation in estimating ballistic property of composites.

6.4 Conclusions

Experimental studies on UT-Composite and VT-Composite were tested against Underwriters laboratory level 1 and level 6 velocities to sustain impact from a 9mm 124grain full metal jacket projectile. Observations made in research are reported with respect to impeding velocities and damage of composites. All the material systems that were designed survived level 1 velocity range. For the same thickness, the composites tested survived level 6 minimum velocity of 426m/s. However, 25UT, 75UT and 25VT showed better performance in surviving against the level 6 maximum velocity of 469m/s. When compared to control, 25UT, 25VT, 75UT and 75VT showed increased performance. At 1wt% loading levels, the composites showed drastic decrease in impeding velocity values. There was not much variation in thickness, areal density and density for alumina nanofiber modified composites and hence no major contribution of the parameters towards ballistic impeding velocities. Surface treatment resulted in strengthening of matrix and hence the composites were stiffer as observed from the cone height formed and resultant post damage sectioned digital images. The damage mechanisms as observed in maximum impeded velocity composite laminates include indentation on the top surface, shearing of fibers in path of projectile, delamination, and dishing. Cross section images of impacted laminates show that failure mechanism is same for all types of material systems. The damage spreads in the form of delamination when projectile is inhibited and is major energy absorption mechanism apart from cone formation. When the projectile penetrates composite, the delamination is more localized to path of projectile. The composite laminate when perforated observes tensile and shear failure in

primary yarns and cracking, delamination in secondary yarns. The plastic deformation of projectile is observed when it meets composite.

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7. CONCLUSIONS AND FUTURE WORK

The research findings made significant and original contributions in terms of understanding the novel unexplored ANF for their effectiveness in resin and composites. The resin formulations with loading concentration of 0.25wt%, 0.5wt%, 0.75wt% and 1.00wt% of untreated (UT) and vinyl surface treated (VT) are considered for their effectiveness on physical, mechanical properties and low velocity impact properties in base resin and E-glass woven reinforced composite. The developed composites were tested against UL-752 Level-1 and Level-6 velocity range to characterize their response.

1. Three roll mill provided high shear forces which efficiently debundled ANF by maintaining the aspect ratio as observed from TEM. Dispersibility studies indicated agglomeration issues for UT-Resin at higher loading levels, but homogenous dispersion can be achieved with VT.
2. The resin physical properties and resin, composite static mechanical properties are compared. The tests revealed that 25VT formulation results in significant enhancement of properties. Incorporation of ANF increased the ability of composite to absorb more energy elastically and deform plastically contributing to higher energy absorption before failure.
3. The fracture analysis revealed VT enhance interfacial binding strength of the modified resin with glass fiber, indicating effectiveness of surface treatment. The efficient interfacial adhesion as observed for 25VT – Composite directly contributed to enhanced properties for the respective composites. The higher void content with the increase of loading content is considered to influence the unpredictable behavior of composites under loading.

4. The low velocity impact study at 135J, 170J, 205J and 240J revealed the enhancement in peak load manifested, energy absorbed, and increased delamination threshold loads for 25VT formulation.
5. The addition of ANF influenced the impeding ballistic velocities. All systems designed exceeded UL-752 level 6 minimum velocity of 426m/s. 25UT, 75UT and 25VT showed highest performance surviving UL-752 level 6 maximum velocity of 469m/s. Increasing in loading level of ANF above 0.75wt% drastically reduces the ballistic resistance performance and this can be attributed to higher void content in the respective composite.

In summary, it can be concluded that glass fiber composite impregnated with 25UT will offer optimal ballistic impact resistance against UL level 6 velocity, with an average areal density of 1.46 ± 0.03 g/sq.cm. A commercial panel with a UL-752 Level 6 rating has a thickness of 9.5mm and areal density of 1.9 g/sq.cm, whereas the composites studied in this research have a thickness of 7.2mm and areal density of 1.4g/sq.cm. The commercial panel for level 6 rating weighs approximately 1748g, the developed composite weighed approximately 1325g. The developed composite could potentially save 25% in weight.

The developed composite panels when used for applications such as troop carriers, medium tactical vehicles, navy vessels, prisoner transport vehicles, robotic ballistic shield and riot shields can provide desired protection at reduced weight. The reduced weight adds indirect advantage of increasing mobility and reduced fuel consumption. Whereas in applications such as safe rooms, guard shacks, weapons facilities, court houses, educational facilities, embassies and consulates, storm and

tornado shelters to name a few can be retrofitted with these composite panels for added protection. If we consider adding the additional weight, then there is a possibility for more profound ballistic resistance capacity of designed composite.

7.1 Future work

The main objective of finding effectiveness of ANF and surface treatment in static, low velocity impact and ballistic impact are realized. Further understanding of composite behavior under ballistic impact loading can be facilitated by testing 12in x 12in sized composite. Estimating operational costs, procuring costs and manufacturing costs can give a direction towards commercialization efforts. Investigating the feasibility of scaling up the manufacturing process particularly dispersion to mass produce composites.

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