Evaluating the effect of nano-particle additives in Kevlar[®] impact resistant composites

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Abstract

Kevlar[®] 29 impact resistant composites are commonly employed for a wide range of applications including ballistic resistant armor. Advancement in the composite's energy absorption and the reduction of weight are critical for increasing their effectiveness in application. Carbon nano-tubes and nano-sized core shell rubber particles are added for thermoset resin systems to enhance toughness and energy absorption. V_{50} ballistic testing was conducted on three classes of Kevlar composites and their energy absorption characteristics were evaluated with a ballistic impact testing and post shot Raman spectroscopy. This study showcases the influence of nano-particle additives on the energy absorption of the composite *via* the Kevlar[®] 29 fibers corresponding residual Raman spectral shifts. Investigating both the $1,611\text{ cm}^{-1}$ and the $1,649\text{ cm}^{-1}$ reference Raman bands, a discussion of as to how the additives are enhancing energy absorption and overall composite performance is presented as well. This work indicates that different mechanisms employed by the two different nano-additives enhance V_{50} ballistic performance by 7.3 per cent and 8 per cent respectively over baseline panels with a 1 per cent weight addition of nano and micro-sized particles by matrix toughening, cavitation, and strengthening the fiber-matrix interface.

Keywords:

D) Raman Spectroscopy, A) Particle-Reinforced Composites, C) Damage mechanics, A) Nano particles, A) Aramid fibre, B) Impact behavior

1. Introduction

Kevlar[®] composites have a wide range of application in both defense and commercial industries. These applications, including ballistic armor and shielding, require balancing weight minimization to the added strength afforded by the composite. These composites allow for energy to be absorbed

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through elongation of the polymer fibers as well as delamination in system with multiple stacked layers [1, 2, 3, 4, 5]. These Kevlar[®] composites are commonly used due to their excellent strength to weight ratio and their ability to absorb a high degree of impact, even from ballistics.

The amount of energy absorption in delamination and through crack propagation of the resin matrix impacts the amount of the stress wave transferred into the fiber reinforcement for composite armor. The mechanism of energy absorption during the crack propagation is also strain rate sensitive [6, 7, 8]. The higher the energy and shorter the duration, the faster the energy absorption mechanisms must function in order to avoid failure. The addition of filler particles in the resin matrix can enhance the toughness and energy absorption characteristics, and particle reinforcement can be of various sizes and morphologies. A theoretical understanding of toughening mechanisms in resin systems has been evaluated through several reviews, and continues to be evaluated [9, 10].

Ballistic testing of composite armor panels with nano-scale additives have been limited to date, however the experiments and simulation that have been conducted have shown great promise [11, 12]. In order to understand the performance of the composite in the field, it is desired to provide realistic testing. As such, composite armor panels were manufactured and prepared for testing at a firing range. The use of high speed imaging and post shot visual and microscopy investigations were designed for as well. Particularly of interest is how the additives influence the load transfer to the fiber weave [13]. As Kevlar[®] 29 is Raman active, the additives influence can be observed by comparing the variations in the characteristic spectra of the fibers.

Raman spectroscopy is a technique used to study vibrational, rotational, and other low-frequency modes in a system [14]. Cen et al [2] focused on Kevlar[®] 29, while the work by Washer et al [15] is based on Kevlar[®] 49. The K49 fiber structure has larger crystallite size resulting in lower total crystal surface area, and has a higher orientation angle of the crystalline structure resulting in a 50 per cent higher modulus than K29. The band shifts are a result of elongation or contraction of the bonds between the molecule's constituents. The 1,611 cm^{-1} band shifts due to stretching in the C-C phenyl ring, while the 1,649 cm^{-1} band shift results primarily from stretching of the C=O with smaller contributions from the C-N and N-H bonds [16]. A presentation of the theoretical and experimentally identified Raman Peaks for Kevlar is presented in Table 1. New work by Grujicic et al. with molecular dynamics for Kevlar[®] chains has simulated the response to loading, including the inter-chain reactions [17, 18]. This has helped understand the load transfer inside the chains. This study looks to understand the energy absorption characteristics of both core shell rubber nanoparticles and multi-walled carbon nanotubes infiltrated for additives for composite Kevlar[®] ballistic armor. Evaluation of these different mechanisms responsible for improved ballistic performance will be conducted in post-shot measurements and ex-situ Raman spectroscopy.

2. Experimental Procedure

The study contains two primary experiments. The study utilizes V₅₀ Ballistics Testing and post shot Raman for characterization. In conjunction, the studies will show the nano-sized additives' effectiveness to increase the performance of the composite under extreme testing conditions, and their influence on the load transfer response of the system.

2.1. Materials

2.1.1. Kevlar® 29

Kevlar® 29 is a polymer chain of Poly-paraphenylene terephthalamide, produced by the reaction of para-phenylenediamine and terephthaloyl chloride. During manufacturing, the fibers are pulled, thereby orienting the polymer chains in the loading direction. Commonly the fibers are spun yielding very high tensile strength [19, 20, 21]. An overview of some of the materials properties is presented in Table 2.

The polymer chain is presented in Figure 1, with a single chain denoted in bold. The polymer chains are compiled into thin sheets, which are then combined in a radial fashion to form a cylindrical Kevlar® fiber [21]. This build up, as well as a sample of the pristine fiber weave, are presented in Figure 1.

2.1.2. Multi Walled Carbon Nanotubes

Multi-walled carbon nanotubes (MWCNT) as supplied by Arkema were utilized for experimentation as an additive to the composite. The Graphistrength® CS1-25 MWCNT for epoxy dispersion in masterbatch form at 25 per cent concentration was utilized. These MWCNT's have diameters up to 100 nanometers, and lengths up to 100 μm . They have the following properties: a specific gravity of 2.90 g/cm³, an apparent density of 0.15 g/cm³, a surface area between 100 and 250 m² per g, and a tensile modulus on the order of 103 GPa.

2.1.3. Milled Carbon Fiber

The Kureha KRECA KGF 200 M-201F milled carbon fiber was manufactured by Kureha in Tokyo, Japan. It was produced with an average diameter of 12.5 μm and an average length of 0.15 μm . Due to their high affinity for resins, no sizing agent was required to ensure the bonding characteristics with the Bisphenol-A based epoxy resins.

2.1.4. Core Shell Rubber Particles

Kane Ace® MX 153, a polymer ball manufactured by Kaneka, was utilized throughout experimentation and is a 33 per cent concentrate core shell rubber (CSR) toughening agent in unmodified liquid epoxy resin based on Bisphenol-A. The diameters of the CSR particles are approximately 100 nm. As an additive the polymer ball is known to have excellent properties to

dissipate energy, acting as a crack terminator. This relieves inherent stresses generated during the resin curing process [22, 23].

2.1.5. Epoxy Resin

The epoxy resin utilized for this research included a bisphenol A reacting with a modified cycloaliphatic amine hardener. Rhino Epoxy 1403 bisphenol-A based resin with Rhino 4120 hardener was utilized for experimentation. The 1403 resin is a medium viscosity, undiluted, extended pot life epoxy resin with a viscosity of 7,300 cPs. The 4120 hardener is a modified cycloaliphatic amine hardener.

2.2. Processing Methods

2.2.1. Dispersion of Nano Particles

The Thinky ARE-310 planetary centrifugal mixer was utilized for dispersion of the nano-particles in the resin systems. Thinky planetary centrifugal mixers are useful for their simultaneous processing of mixing, dispersion, and deaeration of high-viscosity materials. The centrifugal force of over 400g enables thorough mixing, and subsequent deaeration removes any bubbles formed during the mixing process. Mixing cycles were run at 2,000 rpm, and deaeration cycles were run at 2,200 rpm. Dispersion of the Arkema Graphistrength[®] MWCNT's was completed by measuring the appropriate amount of MWCNT's in pellet form and placing in the appropriate amount of Rhino epoxy 1403 resin. This mixture was then inserted in an oven at 100 °C, for at least 12 hours prior to mixing. The heated mixture was then placed in the Thinky planetary centrifugal mixer for a total of ten minutes of mixing with subsequent two minutes of deaeration. Dispersion of the Kaneka CSR particles was done by mixing the specified ratio of nano-particles to Rhino epoxy 1403, and running the mixture through a single cycle of five minute mixing and followed by one minute of deaeration to ensure ideal dispersion.

2.2.2. Impregnation of Kevlar[®] fabric with nano-particle enhanced resin

Impregnation of the BGF 5745 woven Kevlar 29 was accomplished through the use of a Binks 18⁰⁰ (45.72 cm) impregnation machine. The gap on the pinch rollers were set to 0.010⁰⁰ (0.254 mm), which controlled the amount of resin content on the finished product. Each ply of material in the finished part was individually impregnated, and was weighed prior to and after wet-out to have measurements on resin content prior to cure in the autoclave. Average resin content for the V₅₀ ballistic testing was 18.75 per cent with a standard deviation of 0.89 per cent.

A variety of compositions of the additives were investigated, with the content of milled carbon fiber and nano-particle additives ranging between zero and two per cent. Specimens were denoted by the naming conventions such as: additive name – milled fiber weight percentage – nano-particle weight percentage. For clarity, CNT 2-1.5 represents a Kevlar[®] 29 composite with 2 per cent milled fiber and 1.5 per cent multi-walled carbon by weight.

2.3. Testing and Evaluation

2.3.1. V_{50} Ballistic Testing

Thirteen panels of approximately $18^{00} \times 18^{00} \times 0.310^{00}$ (45.72 cm $\times$ 45.72 cm $\times$ 0.78 cm) of 16 distinct plies of 5745 Kevlar[®] 29, impregnated with epoxy at an average resin content of 18.75 per cent with 0.89 per cent standard deviation, were sent to the Oregon Ballistics Lab in Salem, OR for V_{50} ballistic testing as per Military Specification MIL-DTL-662 F [24]. The experimental techniques followed closely with the previous work reported on the subject [25].

The samples were tested in an indoor range with the muzzle of the test barrel mounted 16.5 feet (5.02 meters) away from the target panel and positioned to produce 0 degree obliquity impacts. Four Oehler Model 57 infrared light screens, in conjunction with time-based frequency counters, were positioned such that bullet velocity was measured 8.25 feet (2.51 meters) from the target. Penetrations were determined by examination of a piece of 0.020^{00} (0.508 mm) 2024-T3 aluminum mounted 6^{00} (15.24 cm) behind and parallel to the test sample. All panels were tested utilizing a .44 cal (11.176 mm) Mag 240 grain SWCGC (Semi-Wadcutter Gas Check) bullet, fired from a universal barrel holder utilizing a 10^{00} (25.4 cm) 1:20 .44 cal (11.176 mm) Magnum barrel. The amount of gun powder was varied to adjust the projectile velocity. The ballistic limit is calculated by taking the average of the highest partial and lowest completely penetrating impact velocities [24]. If this projectile is seen to be a partial penetration (i.e. did not pass fully through the panel into a witness panel placed behind the tested panel), the next projectile is shot at an increased velocity [24, 25]. Post shot visual inspection was also conducted examining the degree of delamination of the composite as well as the entrance and exit zones. This is presented in Figure 3a.

2.3.2. Raman Spectroscopy

Raman spectroscopy was conducted to scan the Kevlar[®] composite following V_{50} testing to investigate the residual state of the fibers and understand the influence of the additives. A Renishaw RM-1000 Ramascope with a 1800 groove per mm grating was employed by way of a fiber optic probe with a 50x Nikon objective. A green 532 nm diode laser with 9 mW of power was utilized to excite a Raman response. Measurements were conducted following calibration of the equipment with crystalline silicon, which has a sharp and well researched Raman band peak at 520 cm^{-1} of high intensity. From literature [16, 2, 26], the peaks of investigation were identified at approximately $1,611\text{ cm}^{-1}$ and $1,649\text{ cm}^{-1}$. Spectroscopy readings were conducted on the pristine fibers and compared with literature for agreement, and the measurements were conducted utilizing a portable spectrometer with specification available in published work [27].

For the baseline panel, a 6 $\times$ 6 map was measured encompassing the hole with a scanning area of approximately 25 $\times$ 25 mm. The scanning region is presented in Figure 3b. A total of 36 data points were collected of varying intensity and noise for the baseline panel. Measurements conducted on the edge of

the sample were delineated to see the variance of the scanned region closer to the bullet. One particular challenge for the mapping procedure is due to the impact zone's curvature, where remaining in tight focus becomes very difficult. For the additive panels, collection of Raman spectra was considerably more challenging. The additives present in the matrix showcased a great deal of background fluorescence. As such small, tightly packed scans of 8 points were collected sufficiently away from the bullet hole's curvature to identify the residual stress effects with the use of manual refined focusing for each measurement. This is presented in Figure 3c. The scanning techniques are continuing to be improved in an effort to develop complete contour maps of the impact region. The techniques have shown great promise for large scale spectroscopic stress mapping [27].

3. Results and Discussion

3.1. V_{50} Ballistic Testing

The baseline composite panel and 12 additive variations were examined for their V_{50} impact resistance performance following the MIL-DTL-662F standard [24]. Post shot visual inspection was also conducted examining the degree of delamination of the composite as well as the entrance and exit zones. This is presented in Figure 3. The resulting V_{50} ballistic impact resistance performance as measured in (feet per second) and has been converted to SI unites. It is presented in a tabular format in Table 3. It can be observed that all loadings of nano-particles and milled fiber showed improvement in V_{50} ballistic performance, with the exception of 2 per cent milled fiber with 1.5 per cent MWCNT (CNT 2-1.5). These panels showed equivalent results to baseline panel's performance. The additive panel with 1 per cent loading of CSR and 1 per cent milled fiber (CSR 1-1) had the most increased performance with an 8 per cent improvement, while the additive panel with 1 per cent MWCNT with 1 per cent milled fiber (CNT 1-1) had the second highest performance with a 7.3 per cent improvement. These are significant improvements from the baseline composite with minimal weight addition.

The additive panels with 1 per cent loading of milled fiber showed consistent improvement from the baseline, and were selected as the optimum level of milled fiber additive. Both the CNT 1-1 and CSR 1-1 panel had similar improvements between 7 per cent and 8 per cent over the baseline. This is particularly interesting, due to similar estimated results through computer simulation by Grujicic et al [12], utilizing multi-walled carbon nanotubes for .30 cal (7.62 mm) fragment stimulating projectiles (fsp) ballistic testing. These idealized computed simulations showed a 6.5 per cent improvement in V_{50} ballistic performance. Isolating the nano-particle additive influence without the milled fiber additive by testing the CNT 0-1 and CSR 0-1 additive panels, an improvement of 5.6 per cent and 5.2 per cent respectively was observed. The increase in V_{50} velocity for the additive doped panels referenced from the baseline panel's result is presented in Figure 4. Here the trends for each additive class are more easily identified, with marked improvement for 1 per cent addition of milled fiber further bolstered by

the nano-particle additives. SEM imaging was conducted on the neat and nano-tube additive composites, as seen in Figure 5a and b.

In order to evaluate whether the energy absorption is coming from the elongation of the Kevlar[®] fibers or from the crack propagation through the resin system, an analysis of the back face deformation for the panels is required. Using tick marks as a reference, measurements of the back face deformation can be obtained for each panel post shot. Taking into account movement of the panel, all three panels showed a back force deformation of approximately 1.13⁰⁰ (2.87 cm) as seen in Figure 5c,d,e. Because the back face deformation and therefore the Kevlar[®] fiber elongation is similar for all three panels, the additional energy absorption leading to superior ballistic resistance performance is coming purely from the amount of energy absorbed during crack propagation through the resin matrix. Previous reported work had identified the addition of milled carbon fiber and carbon nano-tubes resulted in a tearing failure of the epoxy [25], rather than a brittle fracture. In this study Raman spectroscopy was conducted to understand the influence of both additive classes mixed with milled carbon fiber filler and the residual state of the fibers in an effort to shed light on the energy absorption mechanisms.

3.2. Raman Spectroscopy Study

Raman spectroscopy was conducted to evaluate the residual strain in the fibers of the various panels. Strain in the sample has been shown to cause a Raman shift, and can be measured via spectroscopy with calibration. Raman Spectroscopy data was obtained post shot and was conducted on the baseline panel and two of the best performing additive enhanced panels, the CNT 1-1 and CSR 1-1. Multiple measurements were taken on each panel post shot and compared with an unstressed pristine Kevlar[®]

29 woven sample as a control. The raw spectra for each tested specimen is presented in Figure 6. These tabulated results are presented in Table 4 and compared with values from literature. The tabulated data identifies the residual state of the fiber by measuring the wavenumber shift for each peak location and comparing them to the pristine fiber sample for reference. Knowing the ballistic resistance performance, the Raman shifts can be compared between the composites to identify the role of the additives on the energy absorption. One finding of interest is the CSR 1611 cm⁻¹ bandshift compared to that of the CNT shift, which is induced by the phenol ring stretching. Both additives showed a marked improvement in ballistic performance, corresponding to 8 per cent for the CSR and 7.3 per cent for the CNT additive panels. For clarity, the tabulated data is presented in Figure 7. In Figure 7, the shifts for both additives are clearly evident. For the Raman bandshift referenced to 1611 cm⁻¹, we can identify that the baseline panel shifts downward from the pristine fibers reference. This is due to partly to the manufacturing and curing process in addition to the impact loading. This baseline or neat composite was the control for ballistic resistance V₅₀ measurements. As expected, the CNT panel shows a further downshift in the Kevlar[®] fiber's response, which correlates with the increased ballistic impact

resistance observed. Conversely, the CSR additive panel reports an upshift in the Kevlar[®] Raman response which is indicative of a decrease in fiber strain. However, it too showed even greater ballistic impact resistance performance.

In an effort to understand the phenomenon more completely, a secondary band in the fiber was examined at 1649 cm⁻¹. In Figure 7 we again see a different effect for the secondary band as compared with the primary. As expected the baseline panel showed a downshift from the pristine fiber analysis, with the downshift reporting more significantly in the secondary band. The CNT additive panel downshift is appreciably reduced as compared to both the baseline measurement and CNT additive composite at 1611 cm⁻¹. The CSR additive panel shows a downshift for the secondary band. A clear distinction is identified when comparing the additives' influence for both Raman bands, suggesting that two load transfer mechanisms are involved.

3.3. Discussion

The previous work had shown a change in the epoxy matrix's cracking and failure due to the enhancement via carbon nanotube additives [25]. This work expands the scope by looking at both MWCNT and CSR nano-particles at three different loading levels to look at how the combination of micron and nano-sized particles can improve ballistic performance by enabling distribution of the stress wave down to the energy absorption mechanisms of the nano-particles through the micron sized particles. Isolating the variables for study, such as the class and volume percentage of the additive, ballistic testing was conducted to identify the composite's ability to absorb the energy of a ballistic strike. From the V₅₀ standard testing, an increase of energy absorption was identified and the highest performing additive mixture weight was selected for additional Raman testing. Having conducted the ballistic tests on both the neat and doped panels, it was well concluded that the addition of minimal weight nano and micro-scale additives resulted in an appreciable change in energy absorption showcasing 7.3 and 8 per cent increased ballistic resistance performance as compared to the tested neat panel. The expectation was that the additive panels Raman results would show a similar shift in peak center, with a marked difference from the baseline.

With an understanding of the molecular structure of Kevlar[®] and the corresponding bonds yielding the 1611 cm⁻¹ and 1649 cm⁻¹ bands, a more complete view of the role of the nano-particle additives on the residual stress state can be gained. The DuPont Technical Guide shed light on the formation and molecular structure of the fibers. [21] Figure 8 details the build up of the composite and relates the molecular structure to the Raman spectroscopic measurements. The spectroscopic measurement varies with the strain in specific bonds in the molecular structure [16, 26]. Figure 8 (*Right*) shows how these bond strains are oriented in relation with the molecular sheet, and also (*Bottom*) shows the orientation of the molecular sheets to the individual fibers.

Raman residual state testing revealed that although the increased ballistic performance between the two classes of additive doped panels was nearly consistent, the influence on the Kevlar fiber's Raman peak, and subsequently the residual strain retained by the fiber, were not the same. Compared to the neat panel's Raman results, the CNT additive panel showed an increase in residual strain via the Raman shift and the CSR panel showed a decrease. This was identified in the wavenumber shifts from the primary 1611 cm^{-1} phenol ring activated Raman peak chain, and is also indicative of the axial fiber strain. Secondary bands were investigated including the 1649 cm^{-1} peak, primarily from stretching of the C=O with smaller contributions from the C-N and N-H bonds. These secondary molecular bonds are linked in the radial direction of the Kevlar chains, linking each axially aligned chain together. Both classes of additives were observed to have a marked decrease in the residual Raman shifts from the neat panel's Raman testing. The chain can also be viewed as indicative of the fiber and matrix interaction. These observations suggests that the core shell particles are absorbing and redirecting the impact and crack propagation through deformation, debonding, and cavitation in the matrix. These effects have been studied by scanning electron microscopy, atomic force microscopy, and simulation in related literature [28, 29, 30, 31, 32]. Prasad and Grubb present the frequency shift per unit stress, a calibration for assessing the Raman spectroscopic shifts, as $dv/d\sigma = -2.44\text{ cm}^{-1}\text{ per GPa}$ [26]. Using that calibration, the area averaged change in residual stress from the pristine fiber condition is presented for the Baseline Composite (436 MPa), CSR Composite (-113 MPa), and CNT Composite (582 MPa).

For future consideration, both additives in conjunction should be implemented to the baseline composite to test for further increases in ballistic performance. The ballistic testing showed particular weight fractions of single additive classes to be quite effective of raising the ballistic resistance performance, and showed that others were not. This decline in performance is postulated to be due to agglomerations and difficulty transferring loading throughout the matrix and then into the fibers. From this assertion, it would be ideal to conduct additional testing with a mixture of the additive classes to identify the joint effect interaction on energy absorption in the system. Due to their minimal weight additions and likelihood for great increases in ballistic performance, this further testing is planned in the future work.

4. Conclusion

Body armor is traditionally made incorporating Kevlar[®] panels. An increase in ballistic resistance with the addition of negligible weight of nano-particles affords either a reduction in composite weight to maintain the same performance or provides a marked improvement in ballistic resistance performance. Several additive enhanced Kevlar[®] composites were tested under high energy impact for V_{50} analysis, along with post shot visual inspection, and high speed imaging,

The additive panels with 1 per cent milled fiber and 1 per cent CSR or CNT additive were shown to exhibit the best impact resistance increases, by 7.3 per cent to 8 per cent respectively over baseline

panels. Raman spectroscopy was conducted and provided insights on the response, damage mechanisms, and load transfer to the fiber weave. These residual measurements on the energy absorbed and retained by the system showed that the CSR nano-particle additive appears to be effective in absorbing energy during impact which resulted in reducing the residual axial stress identified in the fibers, while providing a marked improvement in ballistic performance due to the energy absorption mechanism of cavitation for its particles as described by Yee et al [32]. CNT additives appear to increase matrix fiber interface which was evident in the increased residual axial. This too provided a marked improvement in ballistic performance. This increased residual state can be due to the difference in energy absorption mechanisms for the CNT's defined by Blanco et al [33] as both pullout (frictional sliding) from the matrix or sword-in-sheath sliding. This difference in fiber axial loading may be due to the CNT's pullout or sword-in-sheath sliding equate to resin movement and therefore axial loading of fibers in the matrix.

Both core shell rubber particles and multi-walled carbon nanotubes were shown in this study to enhance V_{50} ballistic resistance performance over baseline neat panels with a 1 per cent weight per cent addition of nano and micro-sized particles. The investigation identified that the role of the additive's energy absorption for the composite is different for both classes of additives. For future consideration, both additives in conjunction should be implemented to the baseline composite to test for further increases in ballistic performance, as the mechanisms appear to be unique, non-linear, and could be optimized for high performance gains.

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6. Images & Tables

Figure 1: **Kevlar Fibers:** Molecular structure of Kevlar R (Left), its orientation in a Kevlar R fiber (Center), and Pristine weave (Right)[34].

Figure 2: **Kevlar panels for Raman residual testing:** a) Baseline neat Kevlar R composite, b) carbon nanotube additive composite (CNT 1-1), c) Core shell rubber nano-ball additive composite (CSR 1-1)[34].

Table 1: Kevlar® 29 Raman Properties, Theoretical vs. Experimental Results [2, 35, 36, 15]

Theoretical (cm ⁻¹)		Experimental (cm ⁻¹)					
Penn & Milanovich, Kim et al.		Washer, Brooks and Saulsberry					Cen et al.
		Kevlar R Yarn	Kevlar R Strand				
		647 nm	488 nm	647 nm	752 nm	1,064 nm	633 nm
1,615	1,615	1,613	1,612	1,613	1,612	1,615	1,611
1,649	1,654	1,649	1,649	1,649	1,649	1,651	-

Table 2: Material and mechanical properties of Kevlar® 29, Kevlar® 49, and 5745 Kevlar R weave. [21, 37].

	Spec. Density (g/cm ³)	Tenacity (MPa)	Modulus (MPa)	Break Elongation Per Cent	Spec. Tensile Strength (MPa)	CTE (10 ⁻⁶ per °C)	Decomposition Temperature °C
Kevlar 49	1.44	3000	112,400	2.4	3,600	-3.96	427-482
Kevlar 29	1.44	2920	70,500	3.6	3,600	-3.96	427-482

Style	Weave	Yarn	Count (picks per cm)	Weight (gsm)	Thickness (mm)	Breaking Strength (N per cm)
5745	Plain	3333 dtex Kevlar	0.61

Figure 3: **Post shot examination and scanning procedure:** a) Kevlar® 29 baseline composite following V_{50} ballistic impact testing. Scanning variations between baseline b) and the additive panels c) due to curvature and fluorescence challenges.

Figure 4: **Comparison of V_{50} velocities:** Comparing the baseline composite with both additive composite panels to investigate ballistic resistance performance and energy absorption.

Figure 5: **Imaging studies:** a) SEM imaging on neat composite, b) SEM imaging on CNT additive composite. c, d,

e) Back face comparison core shell carbon additive

deformation for baseline, rubber, and nanotube composites.

Figure 6: **Raman Spectroscopy:** a) molecular structure of Kevlar R, b) raw spectra for Pristine Kevlar R fiber, c) raw spectra for Kevlar R in neat baseline composite, d) raw spectra for Kevlar R in CNT additive composite, e) raw spectra for Kevlar R in CSR additive composite.

Table 3: V_{50} Ballistic Results for Various Loadings of Kevlar® 29 Composites

Sample	Weight (kg)	Thickness (cm)	High Partial (m/sec)	Low Complete (m/sec)	Range (m/sec)	Mixed (m/sec)	V_{50} (m/s)
Baseline	1.823	0.77978	364.23	357.53	12.80	6.70	360.27
CNT 0-1	1.886	0.76454	384.96	371.55	13.41	13.41	379.17
CNT 1-1	1.850	0.77724	392.88	370.94	25.90	21.94	386.48
CNT 2-1	1.837	0.78486	378.56	384.35	14.63	-	380.08
CNT 0-1.5	1.850	0.7874	363.32	363.32	18.59	-	363.32

CNT 1-1.5	1.832	0.78486	376.73	379.78	14.32	-	380.39
CNT 2-1.5	1.837	0.78486	359.96	361.49	9.44	-	359.96
CSR 0-1	1.651	0.77724	391.05	377.64	29.87	13.41	385.26
CSR 1-1	1.855	0.78486	389.53	388.92	19.50	0.60	389.22
CSR 2-1	1.905	0.78486	372.77	373.07	11.88	-	373.68
CSR 0-2	1.710	0.78232	366.97	370.33	16.76	-	371.55
CSR 1-2	1.832	0.77724	384.35	378.56	10.97	5.79	382.21
CSR 2-2	1.832	0.77978	378.56	359.05	21.33	19.50	372.16

Figure 7: **Raman Analysis:** Comparing the additive's effect on the piezospectroscopy results and the associated ballistic resistance performance[34].

Table 4: Resulting peak centers for Pristine, Literature, Baseline, and Additive Panels with statistical data

Sample	Pristine	Cen et al. [2]	Baseline	CSR	CNT
Peak A Center (cm ⁻¹)	1610.942	1611	1609.875	1611.22	1609.52
Standard Dev.: Peak A	0.098	NA	0.179	0.279	0.755
Shift from Pristine	0	-0.058	1.066	-0.278	1.422
Peak B Center (cm ⁻¹)	1648.512	NA	1647.213	1647.845	1647.991
Standard Dev.: Peak B	0.3	NA	0.66	0.809	0.421
Shift from Pristine	0	NA	1.299	0.667	0.52

Figure 8: **Linking the molecular structure and piezospectroscopic measurements to mechanical loading:** *Top:* Molecular structure Raman fingerprint for C-C phenyl ring at 1611 cm^{-1} and C=O/C-N/N-H bonds at 1649 cm^{-1} . *Right:* Kevlar K molecular sheet showcasing strained bonds of interest, including inter-molecular Nitrogen-Hydrogen bond [21]. *Bottom:* Kevlar[®] 29 Fiber with assembled molecular sheet cutaway [34].