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Report Title

STIR: Tailored Interfaces for High Strength Composites Across Strain Rates

ABSTRACT

The objective of this STIR research effort was to study the influence of nanostructured interfaces in the interfacial behavior of polymer fiber reinforced composites such that lightweight materials can be designed for both structural and ballistic performance. To achieve this objective a nanostructured interface has been grown on the fiber surface using a process recently developed by the PI. This process allows for growth at low temperature, which preserves the fiber strength and makes the growth compatible with polymer fibers. This is the first technique for the growth of a reinforcing whisker or nanowire on polymer fibers. The nanowire growth process is highly controllable and acts to enhance the load transfer between the matrix and fiber while also providing out of plane reinforcement. The controllable nanowire growth offer a means for optimizing the interfacial properties such that an ideal material response can be obtained at both high and low strain rates. In addition to control of the nanowire morphology and load transfer, the adhesive bond between the brittle nanowires and the tough Kevlar fiber was varied such that under impact the interface releases the fiber to absorb the ballistic energy.

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Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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09/02/2013 1.00 Hyun-Sik Hwang, Brendan A. Patterson, Mohammad H. Malakooti, Henry A. Sodano. Modification of Pullout Behavior of Kevlar Fabric by Zinc Oxide Nanowire Reinforcement, Proceedings of the ASME 2013 International Mechanical Engineering Congress & Exposition. 2013/11/18 00:00:00, . : ,

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TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

- 2012 American Society for Composites Young Composites Researcher Award

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Hyun-Sik Hwang	0.50	
Brian Davis	0.25	
Brendan A. Patterson	0.25	
FTE Equivalent:	1.00	
Total Number:	3	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Henry A Sodano	0.10	
FTE Equivalent:	0.10	
Total Number:	1	

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Scientific Progress

See Attached.

Technology Transfer

STIR: Tailored Interfaces for High Strength Composites Across Strain Rates

(Proposal No. W911NF-12-1-0362)

Final Report

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1. Research Objectives

The objective of this STIR research effort was to study the influence of nanostructured interfaces in the interfacial behavior of polymer fiber reinforced composites such that *lightweight* materials can be designed for both structural and ballistic performance. To achieve this objective a nanostructured interface has been grown on the fiber surface using a process recently developed by the PI. This process allows for growth at low temperature, which preserves the fiber strength and makes the growth compatible with polymer fibers. This is the first technique for the growth of a reinforcing whisker or nanowire on polymer fibers. The nanowire growth process is highly controllable and acts to enhance the load transfer between the matrix and fiber while also providing out of plane reinforcement. The controllable nanowire growth offer a means for optimizing the interfacial properties such that an ideal material response can be obtained at both high and low strain rates. In addition to control of the nanowire morphology and load transfer, the adhesive bond between the brittle nanowires and the tough Kevlar fiber was varied such that under impact the interface releases the fiber to absorb the ballistic energy.

Soft body armor has also been studied in coordination with Dr. Chian-Fong Yen at RDRL-WMM-B. In this effort we have investigated the effect of the nanowires grown on the surface of Kevlar fibers on the intertow friction formed during pullout. The nanowires act to increase the tow-to-tow friction and thus can be used to improve the energy absorption of a ballistic impact. The objective of this STIR research have been to: 1) develop the functionalization and nanowire growth process such that the interface can be controlled, 2) characterize the interface and tow pullout properties and 3) deliver nanowire treated Kevlar fabric to ARL for testing.

PART 1. EVALUATION FOR HARD ARMOR

The future development of higher performance structures and systems depends heavily upon the use of materials with greater specific strength. Composite materials are an obvious choice as the constituents can be tailored to meet the structure's demands. In particular, a continuous fiber polymer matrix composite offers high strength to weight, high toughness to weight, and design flexibility to match the material with the structural demands. One fiber of commercial and academic interest is the aramid class of fibers (Kevlar[®], Twaron[®]) because the highly crystalline structure offers one of the highest specific toughness ratios and specific strength of common, commercially available fibers.¹ Since the advent of the modern composite materials, our knowledge of mechanical properties of fiber reinforced composite materials has matured, to the extent of accepting prevalently the notion that the quality of the fiber-matrix interface is a crucial factor in many of the composite structure's bulk properties.² Furthermore, a combination of a strong fiber and a well-suited matrix does not guarantee the strong composite since the fiber matrix interface is equally important in determining the overall strength of the composite.^{3,4} As

such, many prominent researchers have investigated methods for improving the interface of modern composite materials. Whiskerization,^{3,4,5,6,7} chemical treatment,^{8,9,10} and plasma treatment^{11,12} have shown promising results for interface improvements; however the fiber's mechanical properties are often significantly degraded resulting in a composite with reduced in-plane properties.³ Poly(p-phenylene terephthalamide) (PPTA) or aramid fibers exhibit chemical resistance due to the high crystallinity of the fiber and the stability of the aromatic carbon atoms (Figure 1).

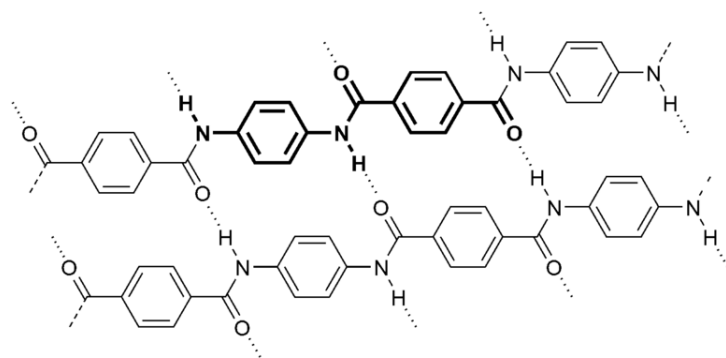


Figure 1. Structure of an aramid (Kevlar[®]) fiber, showing stable aromatic carbon rings attached to backbone chains and hydrogen bonding among the chains, implying high crystallinity.

While this property is advantageous in some instances, woven polymer matrix composites are often limited by a poor interface since the inert fiber will not react with the active groups of the polymer matrix. Therefore, a range of chemical treatments to change the surface groups of the aramid fiber have been attempted with limited success. Most of these chemical enhancements focused on the attachment of primary amine functional groups on the surface of the fiber because primary amines are one of the reactive constituents of thermoset epoxy polymer matrices. Fibers have been functionalized by several processes including nitration,⁸ metalation,^{13,14} organic solvent treatment¹⁵ and plasma functionalization^{11,12} in the past with limited success.

Whiskerization or surface roughening has also been employed to enhance interfacial strength. Creating surface texture increases the surface area for van der Waals bonding and creates a strong mechanical interlock with the polymer matrix. Single crystal silicon carbide or silicon nitride whiskers have been grown on the surface of fibers with great success in increasing the interfacial shear strength. Rabotonov⁵ noted that uniform spatial arrays of whiskers generated the highest improvements in interfacial strength. It was also noted however, that the high temperatures and catalysts required for growth of the whiskers typically damaged the core fiber and reduced the in-plane strength of the composite.³

These investigations were performed on carbon fibers, which can withstand significantly higher temperatures than aramid or other polymer fibers. For this reason, the first whiskerization was only recently achieved by Ehlert et al.¹⁶ using ZnO nanowire arrays. The ZnO nanowire arrays were found to exhibit poor bonding with the aramid fiber and thus a hydrolysis reaction was employed to functionalize the fiber and disrupt the hydrogen bonding in the fiber to create carboxylic acid groups available for interaction with the metal oxide. It was recently found that

the presence of ketones on the fiber surface may be desirable and thus a new functionalization process was developed here that employs a Friedel-Crafts reaction to graft chloroacetone to the fiber surface.¹⁷

1.0 Experimental

1.1 Fiber preparation and functionalization

The Kevlar fibers used in this study were purchased from CST (Tehachapi, CA) and were cleaned in boiling chloroform, acetone, and absolute ethanol to remove the manufacturer applied surface adhesive, followed by drying at 100°C in a convection oven for 1 h. In order to change inert surface of the aramid fiber to be favorable for ZnO nanowire growth and adhesion, two different types of surface functionalization methods; hydrolysis by a strong base (sodium hydroxide) and Freidel-Crafts reaction were used. For the functionalization by hydrolysis of amide bond in aramid fiber, sodium hydroxide was used as a strong base.¹⁶ Fibers were functionalized by soaking in a 10 % aqueous NaOH solution for 20 minutes, followed by subsequent washing with copious amount of deionized water and drying. An ion exchange process was then performed to remove the sodium ion in the carboxylic salt of the functionalized fibers through an acid wash in a beaker of 35% HCl and then rinsed several times in deionized water. The fibers were again dried completely in a convection oven. Another surface functionalization was conducted through Friedel-Crafts acylation, a named reaction in organic chemistry for grafting a variety of functional group onto aromatic compounds. For the Friedel-Crafts functionalization, 13 g of AlCl₃ was dissolved in 100 ml dichloromethane in a nitrogen-filled glove box followed by the addition of Kevlar fibers and 50 ml chloroacetone to the mixture. The fibers were kept inside the mixture overnight until the color of the mixture turned almost black. After the reaction completed, the reaction's residue on the fiber surface washed by Soxhlet extraction, and the fibers were subsequently dried at 100°C in a convection oven. The final product of this Friedel-Crafts functionalization procedure will have ketone and methyl groups grafted on aromatic carbon rings, as shown Figure 2.

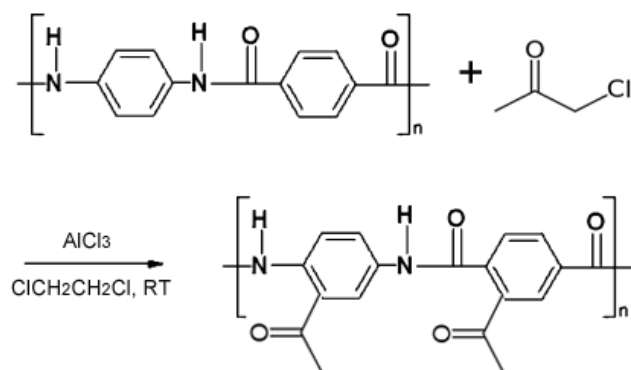


Figure 2. Functionalization of aramid fibers through Friedel-Crafts acylation.

The synthesis of ZnO nanowires on Kevlar was conducted in two steps; an initial seeding process following by the nanowire growth. For the seeding process, the fibers were dipped into a colloidal solution of ZnO nanoparticles (2nm diameter) that was synthesized from 20 mM NaOH and 12.5 mM solution of zinc acetate dihydrate in ethanol, detailed in the work of Ehlert et al.¹⁶ The fibers were then annealed at 150°C to help adhere the nanoparticles to the fiber surface.

This was repeated two additional times. During this seeding step, a thin, conformal, polycrystalline ZnO seed layer is formed on the Kevlar fiber's surface. As the second step, the fabrics were placed into the ZnO growth solution. The growth solution was prepared as an aqueous solution of 25 mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 25 mM hexamethylenetetramine (Alfa Aesar, Ward Hill, MA) in deionized water at 90°C. Fibers were placed in the preheated growth solution for 4 h in a temperature-controlled water bath and then gently washed several times with deionized water. Fibers were then dried at 100°C and prepared for scanning electron microscopy (SEM) imaging. During the second step, ZnO nanowires grow competitively from the seed layer, forming vertically aligned nanowire arrays onto the fiber surface. The scanning electron microscopy of ZnO nanowire arrays on a Kevlar fiber is shown in Figure 3.

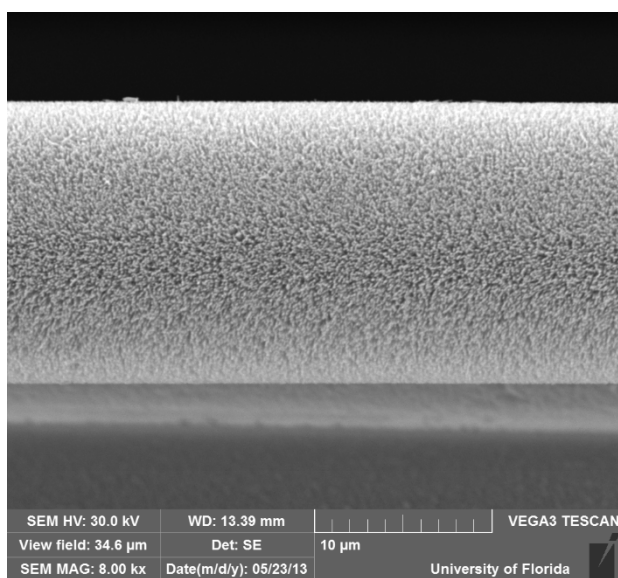


Figure 3. SEM micrograph of aligned ZnO nanowires arrays grown on Kevlar fibers functionalized using a Friedel-Crafts reaction (scale bar 10μm).

2.0 Result and Discussion

2.1 Spectroscopic Verification of Functionalization

The Friedel-Crafts functionalization procedure introduces ketone groups onto aromatic carbon rings of Kevlar backbone chain, as shown in Figure 2. The ketone groups grafted onto the aromatic carbon ring was expected to result stronger bonds between the Kevlar surface and ZnO nanoparticles since the ketone groups which have high-surface energy will not be involved in hydrogen bonding of Kevlar backbone chain (shown in Fig. 1), as will be shown in our single fiber segmentation data.

X-Ray Photoelectron Spectroscopy is a surface chemistry technique that can provide quantitative analysis of the surface chemistry of fibers since it only captures information from the top 2nm of the substrate. The XPS experiments were run at ultrahigh vacuum, $<10^{-8}$ torr, with excitation from an Al $K\alpha$ single anode source. The samples were mounted with a nonmagnetic mask, and charge compensation was performed with a 4 eV flood gun above the sample near the condenser lens. Data analysis, including peak decomposition, was performed in CASA XPS and Matlab. Figure 4 shows the XPS spectra of the Kevlar fibers. The collected

spectra of intensities at various binding energies are decomposed into a sum of Gaussian-Lorentzian distributions centered at various locations. A Shirley background was subtracted, and the peaks decomposed. Peak labels were introduced to show the chemical bonding state associated with the particular carbon. Individual peaks best matched the collected data in the carbon region on the functionalized fiber, which is also consistent with the theorized number. As shown in Table 1, the fraction of ketone increased, as well as introduction of other oxygen-containing group which also would increase surface energy. Increased oxygen-containing groups on the aramid fiber surface suggests that the Friedel-Crafts functionalization did take place on the Kevlar fiber.

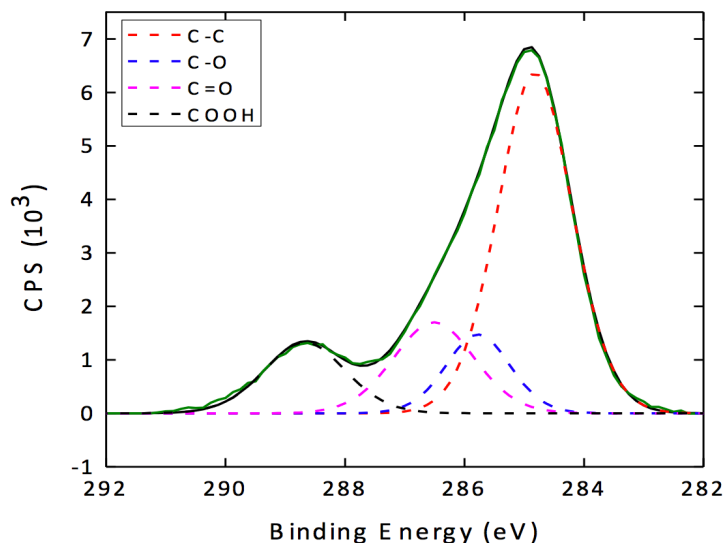
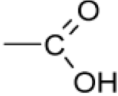


Figure 4. Decomposed bonding states of the C 1s energy region with labeled chemical structures, showing the presence of functional groups on the aramid fiber surface. Table 1 shows the relative fraction of each state.

Table 1. Theoretical and Experimental Bonding State Peak Locations and Concentrations

Chemical Structure	Peak location (eV)	Peak fit (eV)	Error (eV)	Theor. State Conc.	Meas. State Conc.
	284.70	284.88	0.18	85.7 %	58.2 %
C-O	286.5	285.75	-0.75	0.0 %	11.6 %
C=O	287.5	286.50	-1.0	14.3 %	17.0 %
	289.0	288.63	0.04	0.0 %	13.2 %

2.3 Single fiber tensile testing

The ZnO nanowires interphase is designed to significantly improve the interfacial strength in aramid fibers; however, to be effective, it must also preserve the fiber properties so that the composite's in-plane properties are maintained. In order to demonstrate this, single-fiber tensile testing has been performed to characterize the in-plane strength, which is dominated by the

fiber's axial properties. Single fibers of each treatment condition were tested similar to ASTM C-1557 to determine the fiber tensile strength. Single fibers were mounted to paper templates with a 12.7 mm gauge length by epoxy. The fibers were aligned and strained at 8.0 $\mu\text{m/s}$ until failure. Each specimen was examined for linear elastic behavior and a sample of at least 16 fibers of each condition was tested. To comply with established standards, each fiber should be measured after failure. The fiber diameters were measured by SEM to give an average diameter of 11.87 μm . The measured values differ slightly from the nominal diameter of 12.5 μm provided by the manufacturer.

The results of the single-fiber tensile strength are shown in Figure 5. It can be seen in this figure that the strength of the fiber is not negatively influenced by either the functionalization or nanowire growth processes. This result is a major advantage of this work because past efforts for chemical modification of the fiber surface to achieve increased adhesion with the matrix have all seen improved interfacial properties at the cost of the fiber strength. No other current whiskerization technique is compatible with polymer fibers because of the high-temperature processing required. Because our growth process is performed at 90 $^{\circ}\text{C}$, which is well below the temperature at which aramid fiber degrades at, nanowire growth does not affect the fiber integrity. This result demonstrates that neither the functionalization nor growth processes will negatively impact the in-plane properties of the composite.

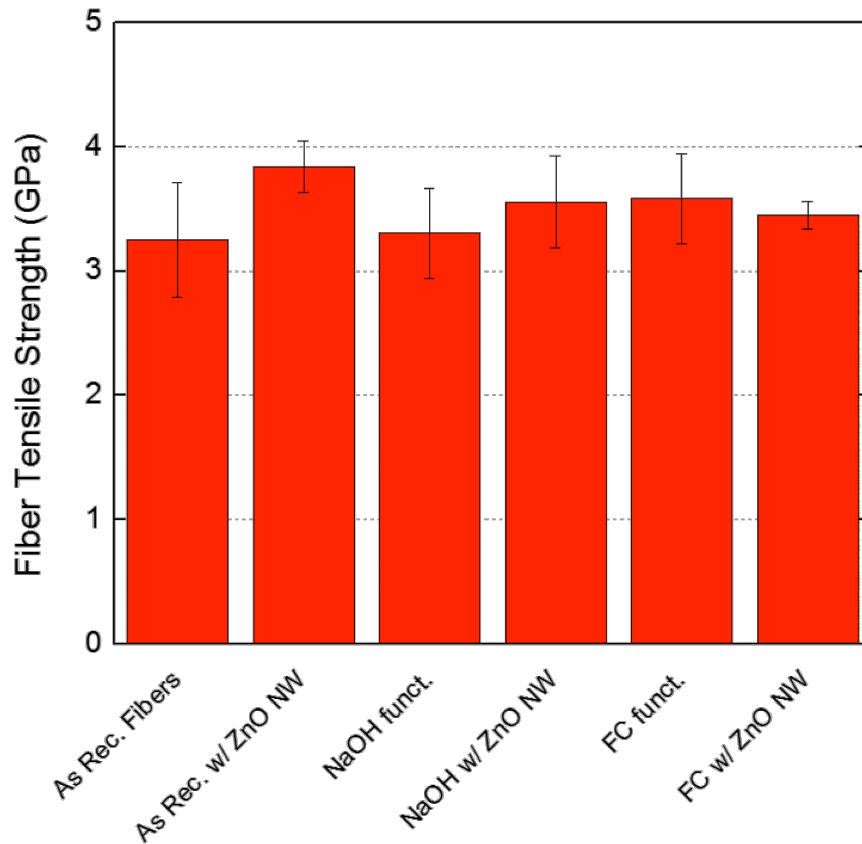


Figure 5. Tensile strength of modified aramid fibers showing no degradation in the fiber tensile strength. The fibers tested were as received, as-received with ZnO nanowires, fibers functionalized by NaOH, fibers functionalized by NaOH with ZnO nanowires, fibers

functionalized by Friedel-Crafts reaction, and fibers functionalized by Friedel-Crafts reaction with ZnO nanowires.

4.2 Single Fiber Fragmentation Testing

The interfacial property of the Kevlar fiber after surface functionalization was evaluated through single-fiber fragmentation (SFF) test, a method that is widely used to assess the properties of the fiber/matrix interface.^{4,16,17} In this test, a single fiber is embedded into a larger dogbone-shaped polymer specimen that is loaded while being observed through an optical microscope. As the specimen is stretched, the fiber will begin to break. The application of more strain causes the fiber to fracture into shorter segments until a saturation point is reached, with each segment transferring load across the interface via shear. At this saturation point, the surface area of each fiber segment can no longer transfer sufficient shear load to the fiber to reach the tensile strength and induce further breaks. Then by measuring the average fragment length, one can estimate the critical length to be

$$l_c = \frac{4}{3} \bar{l} \quad (1)$$

where $\bar{l}$ is the total number of fragments divided by the 16 mm gauge length used in our experiments. The critical length is the length at which the fiber cannot support the load applied through shear across the interface. Using a force balance and the simple shear lag model, one can obtain

$$\tau = \frac{\sigma_f(l_c) d}{2l_c} \quad (2)$$

where $\sigma_f(l_c)$ is the fiber tensile strength and d is the fiber diameter. Thus at constant fiber diameter and fiber strength, more number of cracks imply a stronger fiber/matrix interface, therefore allowing the interfacial strength to be evaluated for the ZnO nanowire coated and uncoated fibers [7]. And the fiber tensile strength at the critical length, $\sigma_f(l_c)$, calculated by

$$\sigma_f(l_c) = \sigma_f(l_o) \left(\frac{l_o}{l_c} \right)^{1/m} \quad (3)$$

where m is the Weibull modulus fitted to the data of $\sigma_f(l)$. This relationship, detailed elsewhere [26], was employed to analyze the fragmentation strength of the data.

Single fiber segmentation testing was based upon the detailed work of Feih et al. [26]. Single aramid fibers were placed in a silicone rubber mold and pretensioned to 15 g. The molds were then filled with a 100:16.9 mixture of Epon 862/Epikure 9553 (Hexion, Houston, TX) and gelled for overnight. Then the half-cured samples removed from the molds and heated in an oven to 100 °C for 1 h, followed by 1 h at 160 °C. Samples were polished and then observed during the tensile straining in a microscope with transmitted polarized light. Finally the samples were strained and then scanned for cracks until the number of cracks in the length of the fiber was saturated. The tensile stage for single-fiber fragmentation testing was designed such that it allows the stress and strain on the specimen to be applied and monitored through an optical microscope under polarized light. The samples were placed in a screw-driven microtensile test stage shown in Figure 6a. Using this system, the number of fragments was measured under increasing strain such that the saturation point could be identified. Figure 6b shows an optical

micrograph of the fractured fiber. The number of fragments was then used to determine the critical length and interfacial strength of the composite. Segmentation tests were performed on bare and functionalized (hydrolyzed, Friedel-Crafts) aramid fibers as well as bare and functionalized fibers with ZnO nanowires grown on the surface. The interfacial shear strength for each of the six cases studied is plotted in Figure 6c. The interfacial shear strength values observed of bare fibers are comparable to those presented in single-fiber fragmentation testing in the literature.¹⁸ The interfacial strength of the functionalized (by Friedel-Crafts reaction) fibers with ZnO nanowires is observed to increase up to 96.9 % over that of the as-received fibers. Moreover, the fibers functionalized by Friedel-Crafts reactions showed 23 % higher interfacial strength than the fibers functionalized through hydrolysis by a strong base.

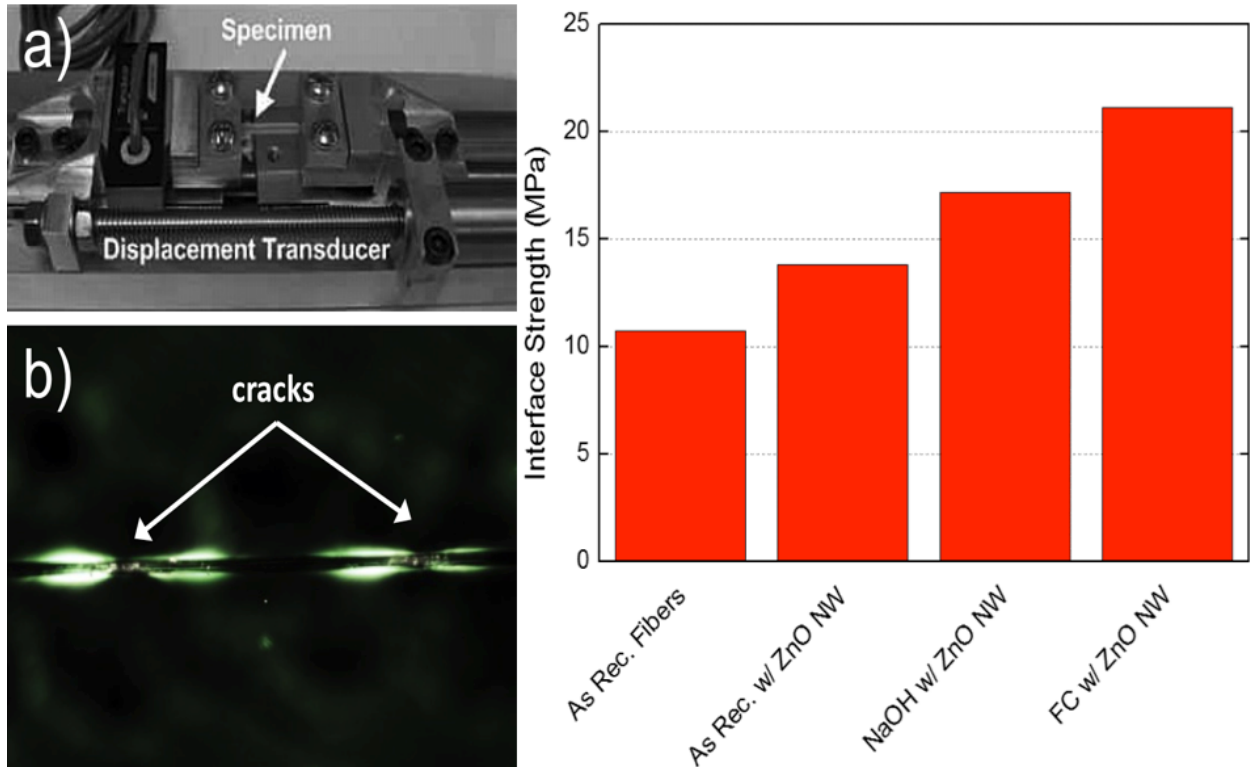


Figure 6. a) Microtensile frame used in the testing with a specimen in jaws. b) Micrograph of the typical fiber cracks as observed in situ during the test c) Single-fiber segmentation results showing up to 96.9 % improvement in the single-fiber interfacial strength. The four fibers tested were as-received, as-received with ZnO nanowires, functionalized by NaOH with ZnO nanowires, and functionalized by Friedel-Crafts reaction with ZnO nanowires.

In conclusion, a novel surface functionalization (Friedel-Crafts) of the Kevlar fiber has been developed for aramid fiber reinforced composites, by enhancing the interfacial property between ZnO nanowire array and Kevlar surface. The successful functionalization onto the surface of the aramid fiber verified by XPS and The interfacial strength has shown to be increased by 96.9 % compared to bare fiber. The result of this effort will provide a new solution for the development of hybrid composites based on lightweight polymeric fibers for use in future structural applications.

PART 2. SOFT ARMOR TESTING

In addition to the composite testing, testing of soft body armor was requested during our kickoff meeting at ARL APG. High performance fabrics including Kevlar, Twaron, Zylon, and Dyneema are used in developing body armor due to their high tenacity and ballistic protection characteristics.¹⁹ When the fabric is impacted by a projectile, it dissipates the ballistic energy through a variety of failure mechanisms such as breakage of primary bond in the fiber's molecules, local yarn rupture, bowing, remote yarn failure, fibrillation, and yarn pullout.¹⁹ Among these failure processes, yarn pullout behavior plays a special role in low velocity impact of a blunt faced penetrator with ungripped yarns. In addition, a major factor governing this pullout behavior is revealed as interyarn friction.²⁰ Thus increasing this interyarn friction would be a plausible way to increase the pullout energy and possibly the ballistic impact performance and should be significantly impacted by the presence of a nanowire surface on the fabric.

Shockey et al.²¹ conducted yarn pullout tests on single tow pulled from a fabric under preloaded tension in the transverse direction. The tests were done on a variety of high performance fabrics including Spectra, Kevlar, and Zylon for various pullout rates. Force-displacement data was recorded, and both warp and fill yarns were pulled from the fabric. Their results presented that the effect of pullout rate is negligible for Kevlar, whereas the effect is bigger on Spectra, and significant for Zylon. Kirkwood and co-workers²⁰ focused tow pullout tests on Kevlar KM2 fabric using a device similar to that employed by Shockey et al.²¹ for more comprehensive set of pull-out data. The effects of transverse tension, fabric size, and multiple yarn pull-outs were investigated based on the load-displacement curves from the yarn pullout test. As a result, a semi-empirical model was established presenting that the pullout energy depends on the length of the sample, the transverse fabric tension, the number of yarns pulled at once, the pattern of the pull, and the distance the yarn is pulled. Moreover in their other work, Kirkwood et al.²² also demonstrated that their quasi-static tow pullout test results could be in conjunction with yarn pullout behavior during ballistic impact by comparison with ballistic tests. They showed interyarn friction of Kevlar KM2 fabric plays a major role in the energy dissipation associated with tow pullout behavior.¹⁹

There has been much research on the modification of interyarn friction for enhanced tow pullout behavior. Briscoe et al. studied the role of surface friction and lubrication of Kevlar fabrics by addition or removal of surface lubricants to achieve different levels of interyarn friction. It was found that fabrics with high friction dissipated larger amount of energy with respect to the fabrics with lower friction.^{23,24} In addition to this, Gawandi et al.²⁵ investigated the effect of coating material and its morphology on Kevlar KM2 fabric surface in tow pullout behavior. Morphology of the coated polymer material was modified by applying temperature and pressure. As a result, the fabric with polymer concentration in the undulation areas shows the best enhancement in pullout energy by increasing the interyarn friction.

There have also been many analytical studies to establish a comprehensive model to explain tow pullout behavior. Valizadeh et al. suggested an analytical model on tow pullout forces in various kinds of fabrics. By measuring the degree of deformation of the fabric during the tow pullout test they could predict crucial parameters in the pullout behavior such as the weave angle variations, the yarn-to-yarn friction coefficient, the normal load in crossovers, the lateral forces, and the opposed yarn strain within the fabric.²⁶ Rao et al. performed tow pullout test on Kevlar

KM2 fabric and tows to calculate the friction coefficient and used it to predict the ballistic impact properties of the fabric.²⁷ Sadegh et al. studied the influence of yarn crimp on the ballistic impact resistance. It was revealed that the fabric subjected to a projectile load shows increased pullout forces due to increased interyarn friction.²⁸

These former research efforts showed the importance of interyarn friction on tow pullout behavior. However, the enhancement of the tow pullout behavior from these approaches was relatively small since the research was mainly focused on the tow pullout mechanics of bare fabrics. Here the growth of ZnO nanowires on the surface of the fibers has been studied to determine the effect of this surface treatment on the tow pull out behavior. Ehlert et al.¹⁶ for the first time employed zinc oxide nanowire arrays as an interface on a polymer reinforcing Kevlar fiber with surface functionalization and demonstrated 51% increase in interfacial shear strength of Kevlar fiber-epoxy composite. Thus, a similar reinforcement mechanism might be applicable to Kevlar fabrics in order to create an interlocking phase between the Kevlar tows causing an increase in the interyarn friction. The tow pullout behavior of Kevlar KM2 fabric reinforced with vertically grown zinc oxide nanowire arrays on the fabric surface is investigated. Tow pullout test are performed on a Kevlar KM2 fabric with zinc oxide nanowires on its surface, and the results of the test are compared with those for the bare fabric without zinc oxide nanostructure.

Material Preparation

The soft body armor testing is typically performed using tow pull out testing which requires the growth of the ZnO nanowires on a Kevlar Fabric, which was accomplished using an approach to limit the homogeneous nucleation of ZnO crystals in the growth solution. The Kevlar fabric used in this study is Kevlar KM2 Style 706 scoured (CS-800) fabric purchased from JPS composite. The fabric was cleaned in boiling chloroform, acetone, and ethanol to remove remaining organic contaminants on the fabric surface and dried in a convection oven. The two functionalization techniques described in Part 1 were then applied to the fabric prior to nanowire growth. The synthesis of ZnO nanowire on Kevlar fabric surface was conducted in two steps; initial seeding and nanowire growth. For the first step, seeding was performed by dipping the fabrics in pre-made seed solution of 1.6mM NaOH and 1mM solution of zinc acetate dihydrate in ethanol. Then the fabrics annealed at 150°C to help adhere the seed layer for the ZnO nanowires. This was repeated two additional times. During the first step, a thin, conformal, polycrystalline ZnO seed layer deposited on Kevlar surface. As the second step, the fabrics were placed into the ZnO growth solution. The growth solution was prepared as aqueous solution of 50mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 25mM HMTA, 8mM PEI, and 0.5M NH_4OH in a closed container. The fabrics were placed in the growth solution and kept at 86°C for 2.5 hours. During the second step, ZnO nanowires grow competitively from the seed layer. The scanning electron microscopy of ZnO nanowire arrays on aramid fabrics is shown in Figure 7. As it can be seen in Fig. 7b, the nanowires are relatively uniform in length and diameter.

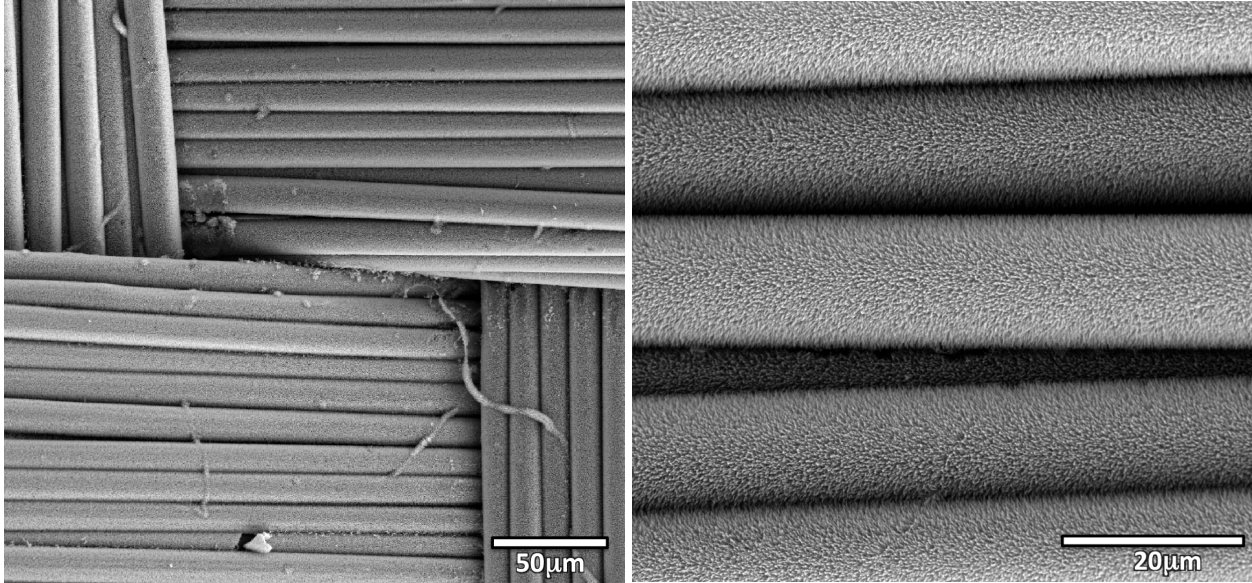


Figure 7. Scanning electron microscope image of ZnO nanowires grown on Kevlar KM2 fabric.

Tow pullout testing is a well reported technique in the literature to correlate yarn pullout behavior of woven fabrics to the ballistic behavior of the material.¹⁹ Figure 7a displays the experimental tow pullout setup. All tests are performed by pulling a single tow from a layer of fabric subjected to the transverse tension. The fabric patch shown in Figure 7b is clamped between a fixed column (7 in Fig. 7a) and an adjustable link (2 in Fig. 7a). The mobile link is equipped with a 100 lb (~445 N) load cell and a lead screw to apply a controlled lateral tension to the fabric. Fabric layers approximately 6.5 inches in width are used to test after manually removing the transverse yarns to provide an overhang of free yarn length of approximately 2.5 inches. The remaining one inch length of the fabric is clamped in the direction of the pull. This length is kept constant for all experiments. The free end of the yarns to be pulled out was glued to a piece of duct tape by an instant adhesive to prevent slippage from the grip during the pullout test. In order to apply the desired preload tension to the fabric, the adjustable knob is rotated to pull the mobile clamp away from the fixed clamp and stretch the fabric in the width direction. A load cell is placed between a movable frame (6 in Fig. 7a) and another fixed column to measure the compression between these two parts which represents the amount of applied

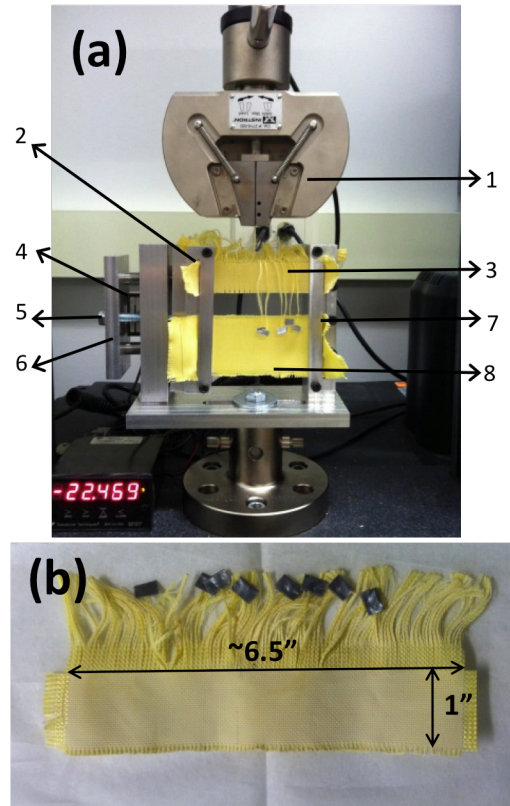


Figure 7. (a) Experimental test setup. 1-grip, 2-mobile link, 3-fabric sample, 4-load cell, 5-lead screw, 6-movable frame, 7-fixed column, 8-dummy fabric and (b) ZnO nanowire grown fabric sample, the ZnO coating can be discerned by the white coating on the fabric however it remains flexible.

tension to the fabric. All tests are conducted using an Instron 5969 machine with a 50kN load cell.

The pullout test performed with one fixed pullout rate of 50 mm/min. Also transverse tension was kept 100 N (~22.48 lb) and a total of 6~8 tows were pulled out from each fabric sample. To determine the number of tows to be left in between subsequent tows being pulled, we referred and verified the work of Shockey et al.²¹ They demonstrated multiple yarns can be pulled from a single fabric without altering the pullout behavior if at least two yarns are in between the successive yarns pulled. Although the observation shows leaving two yarns in between is sufficient, at least five yarns is left between the successive yarns to be pulled in this work. The testing results of four tows pulled from nanowire coated fabric and as received fabric are shown in Figure 9. The as received fibers show a peak load of 7.4 N while the ZnO nanowire coated fibers show a peak load of 48 N or 6.5 times higher friction. The energy absorption can be calculated by integrating the curve and is 10.5 times higher with the ZnO nanowire coated fabric.

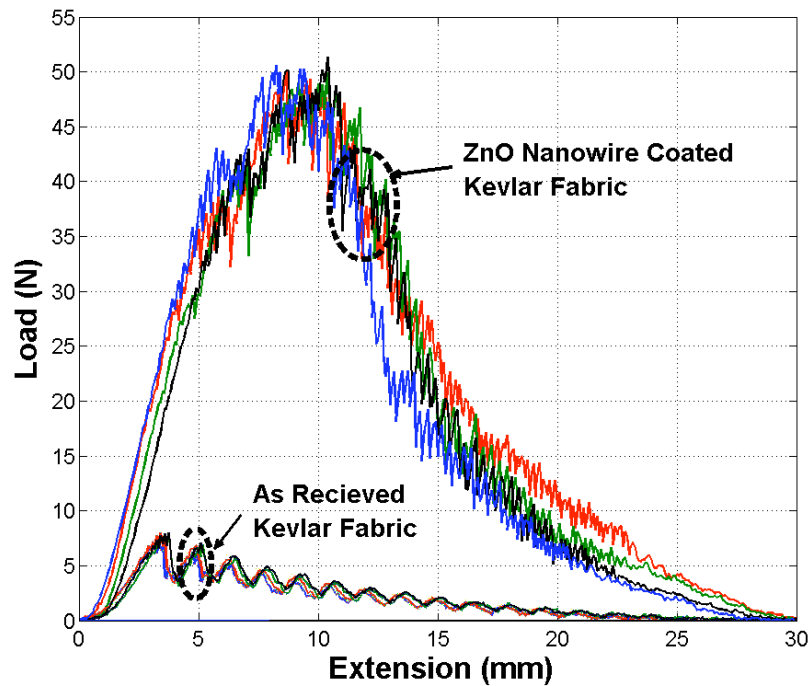


Figure 9. Tow pullout testing on as received Kevlar KM2 and nanowire coated Kevlar fabrics demonstrating 6.5 times higher peak load.

4 Conclusion

In conclusion, a novel surface functionalization (Friedel-Crafts) of the Kevlar fiber has been developed for aramid fiber reinforced composites, by enhancing the interfacial property between ZnO nanowire array and Kevlar surface. The successful functionalization onto the surface of the aramid fiber verified by XPS and The interfacial strength has shown to be increased by 96.9 % compared to bare fiber. Furthermore, ZnO nanowires were shown as a novel approach to increase friction between fabric tows for the enhancement of pullout behavior of Kevlar fabrics has been investigated. The Kevlar fabric was reinforced by vertically aligned ZnO nanowire on each Kevlar fibers, and pullout behavior of the Kevlar fabric with ZnO nanowire was improved

significantly, showing increased peak load up to 6.5 times in pullout test. Pullout properties also could be controlled by using ZnO seed layer and ZnO nanowire layer alternatively, whereas surface treatment including hydrolysis by NaOH and Friedel-Crafts reaction showed no significant effect of surface functionalization. Moreover, it is expected that this enhanced pullout properties of ZnO nanowire reinforced Kevlar fabrics could also improve performance of ballistic impact protection. The result of this effort will provide a new solution for the development of hybrid composites based on lightweight polymeric fibers for use in future structural applications.

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