

## Kevlar-Based Nanocomposites with Hierarchical Structure

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### Abstract

*Stable dispersions of nanoscale Kevlar fibers with diameters between 3 and 30 nm were obtained by deprotonating macroscale, commercial Kevlar yarns with potassium hydroxide in dimethyl sulfoxide. Those aramid nanofibers were surface-treated with phosphoric acid (PA) and glutaraldehyde (GA), and assembled via layer-by-layer (LBL) and vacuum-assisted filtration method into transversely isotropic films. Through Fourier-transform infrared spectroscopy, transmission-electron microscopy, uniaxial tensile testing and thermogravimetric analysis, it was shown that PA hydrolyzes aramid nanofibers which created useful functional groups for surface bonding and GA polymerizes those PA-hydrolyzed nanofibers which served as an inter-fiber crosslinker to improve network properties. A hierarchically structured film made of alternating layers of the high-stiffness, PA/GA-treated, aramid-nanofiber network and high-ductility polyurethane/poly (acrylic acid) was demonstrated to have stiffness and strength exceeding those of commercial Kevlar fiber-woven mats.*

### 1 Introduction

Nature has demonstrated many examples of biological tissues with hierarchical structure leading to exceptional mechanical properties. Nacre, wood and bone are all biological composites with hierarchical architectures to account for their attractive physical or mechanical properties that have inspired the design of microstructures to mimic such properties [1]. Poly-paraphenylene terephthalamide (PPTA), commercialized by Du Pont under the Kevlar trademark, is a high-performance polymer often used in the form of a fiber reinforcement or as a woven mat of fibers. Kevlar fibers at various scales are very stiff and strong which make them good candidates as a matrix material for a hierarchical structure. However, since its invention, the application of Kevlar has been basically limited to fiber reinforcement in a polymer matrix, and the great mechanical properties of Kevlar are realized only along the fiber axes. Kevlar is relatively inert and does not have a strong affinity for most materials used for the matrix of composites, which limits the stiffness and strength of the

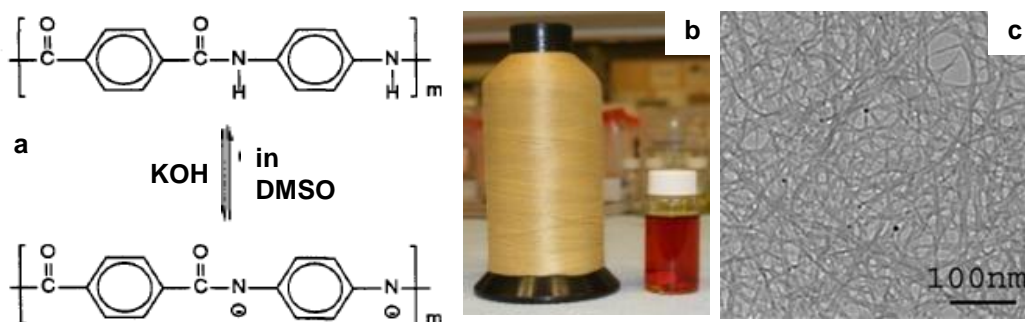
Kevlar fiber reinforced composites, thus they have not found a wide application. On the other hand, the manipulation and tailoring of nanoscale or molecular scale Kevlar have never been studied widely or understood thoroughly.

In this work, we started with Kevlar fibers with nanometer diameters obtained from commercial Kevlar yarns by chemical reactions and designed a Kevlar-based hierarchical structure with excellent mechanical properties. Two length scales were taken into consideration for the design of such a hierarchical structure. 1) Design and tailoring on the molecular level, i.e. Kevlar macromolecules, through phosphoric acid and glutaraldehyde resulted in the control of Kevlar nanostructures and chemical structures as well as their corresponding macroscopic properties. An isotropic, nanoscale, planar structure with high stiffness and strength was achieved by carefully crosslinking Kevlar nanofibers during LBL assembly. 2) Between the layers of this high stiffness and strength nanostructure of Kevlar, a ductile layer comprised of nanostructured polyurethane and poly (acrylic acid) was implemented as a crack deflection weak interface for improving toughness. This layered structure with alternating high and low stiffness materials constitutes a second level of hierarchy and resulted in exceptional stiffness, strength and toughness exceeding the ones of commercial Kevlar fiber woven mat tested along its strongest axis.

## 2 Materials and testing methods

### 2.1 Dissolution of commercial Kevlar fibers in dimethyl sulfoxide

Kevlar was pre-soaked in N-Methyl-2-pyrrolidone (NMP) for 2 days and sonicated. The dispersion of Kevlar nanofibers was achieved by reacting potassium hydroxide (KOH) with Kevlar 69 yarns (from Thread Exchange Inc., right twist) in a dimethyl sulfoxide (DMSO) solution. Figure 1 shows the deprotonation reaction of 1) Kevlar by KOH in DMSO, 2) commercial Kevlar yarns and a solution of Kevlar nanofibers dissolved in DMSO, and 3) deprotonated Kevlar nanofibers dispersed in DMSO. The Kevlar/KOH/DMSO mixture was stirred vigorously at room temperature for seven to nine days until the solution turned viscous and dark red [2].

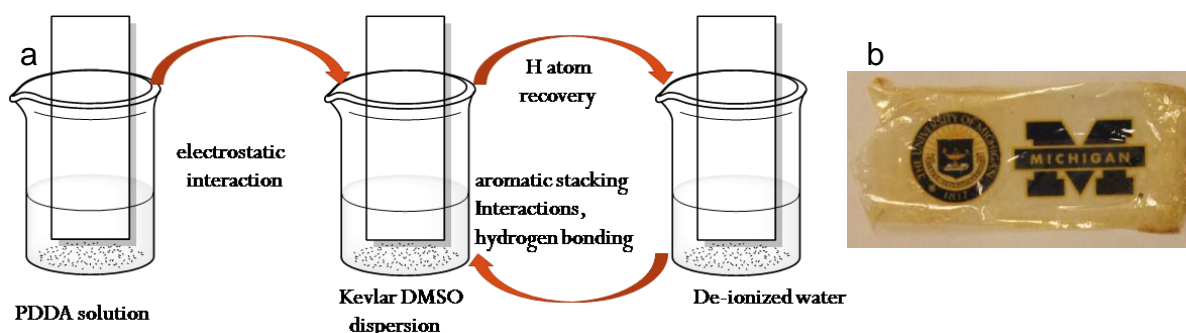


**Figure 1.** (a): The dissolution of Kevlar yarns by KOH due to partial destruction of hydrogen bonding between molecular chains [3]. (b): commercial Kevlar yarns on the left vs. dissolved Kevlar nanofibers in DMSO solution. (c): a TEM image of Kevlar nanofibers dispersed in DMSO KOH solution and deposited on a grid [2].

### 2.2 LBL assembly of PA/GA treated Kevlar nanofiber networks

Layer-by-layer (LBL) assembly is an effective method to prepare nanocomposites with nanoscale control of structure. Previous research has demonstrated the effectiveness of using LBL to achieve high performance nanocomposites due to highly ordered nanostructures [4-6]. PA/GA treated Kevlar LBL films were made by first coating a glass slide with poly

(diallyldimethylammonium chloride) (PDDA) by dipping in 1% PDDA solution for one minute. This first layer of PDDA was necessary for the initiation of Kevlar layer growth since the positively charged PDDA provides an electrostatic attraction to the negatively charged nanofibers. The slide was then immersed in a Kevlar/DMSO solution (of section 2.1) for two minutes, followed by immersion in 10 wt% PA in de-ionized water and 10 wt% GA in de-ionized water for one minute respectively. This process deposited a monolayer of PA/GA treated Kevlar nanofibers on the substrate. The slide was rinsed in de-ionized water for one minute to remove loosely attached nanofibers as well as excess PA and GA, and then dried by compressed air. The process was repeated beginning with dipping in the Kevlar/DMSO solution until the desired film thickness is achieved. As shown in Figure 2, each deposition of Kevlar nanofibers forms hydrogen bonds and aromatic ring interactions with the previously deposited layer. The PA/GA treated Kevlar LBL film is transparent, as shown in Figure 2. Kevlar LBL films without PA/GA treatment were made by omitting the PA and GA immersion steps from the process above. The process of making Kevlar LBL films was automated via a StratoSequence VI machine (NanoStrata Inc.) which was modified by implementing a custom-designed and built robot for using the water-sensitive Kevlar DMSO solution.



**Figure 2.** (a): The process of fabricating a Kevlar LBL film without PA/GA treatment. (b): A transparent Kevlar-LBL film.

### 2.3 Mechanical testing

Uniaxial test for all the samples conforms to ASTM standards D882 which regulates mechanical measurements for thin film with the thickness less than 250 $\mu$ m [7]. Stress-strain curves were obtained by testing ~1 mm wide and 6-10 mm long rectangular strips of the materials with a mechanical strength tester RSA II from TA Instruments (New Castle, DE). Tests were performed at a rate of 0.005 /s strain rate with a ~3.5 N range load cell. The strain was obtained by recording the patterned samples during the test and analyzing afterwards using digital image correlation software Metamorph. The number of tested samples was at least three until repetitive data were achieved.

### 2.4 Film characterization

The thickness of films was examined by FEI Quanta 3D SEM/FIB and Philips XL30ESEM. Loading of the different constituents inside of the free-standing film was determined with thermo-gravimetric analyzer (TGA) Pyris 1 from PerkinElmer; with temperature ramp-up rate of 10  $^{\circ}$ C/min while being purged with air at a flow rate of 20 ml/min. The morphologies of various aramids in DMSO solutions after the PA/GA treatments were obtained using a JEOL 3011 high-resolution electron microscope at 300 kV. One drop of different solutions was placed on the surface of a holey copper grid coated with carbon (Ted Pella) and dried prior to TEM characterizations.

### 3 Results and discussions

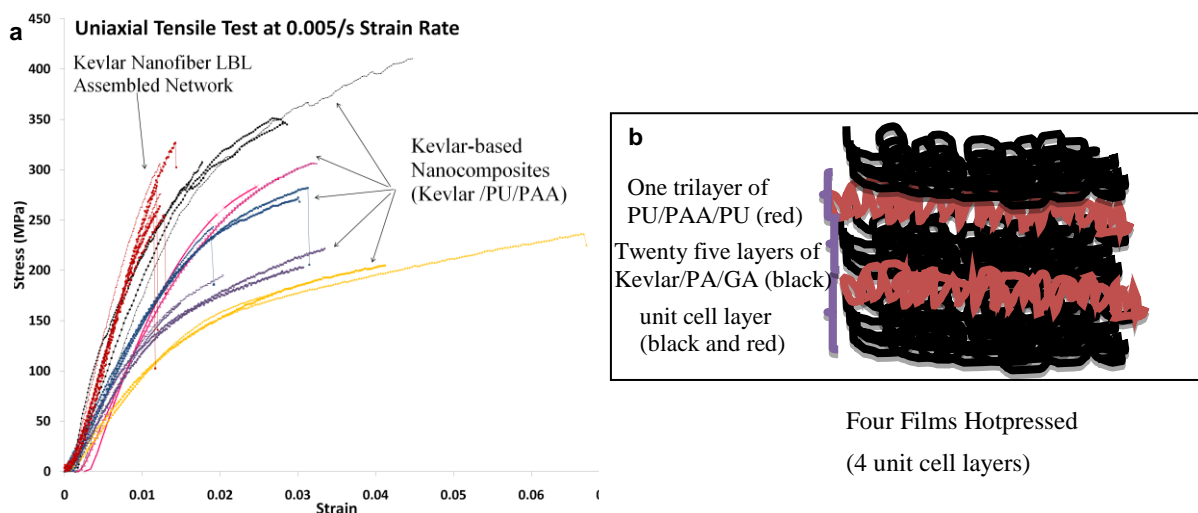
Mechanical properties of the hard Kevlar phase with PA/GA treatment (Kevlar Nanofiber LBL Assembled Network in Figure 3 or NMP-Kevlar/PA/GA in Figure 4) and four hierarchically structured Kevlar samples (Kevlar-based PU/PAA in Figure 3) were characterized via uniaxial tensile tests. Due to different amount of the hard Kevlar phase in the samples, the stiffness of the hierarchical samples varied (Figure 3), as verified by TGA (Figure 4), i.e. the sample with the highest amount of Kevlar had the highest stiffness among the four (Figure 3).

#### 3.1 (NMP-Kevlar/PA/GA)

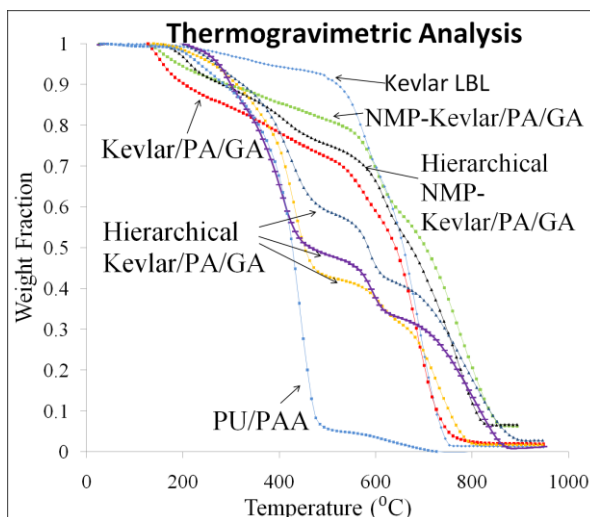
The (NMP-Kevlar/PA/GA) LBL film had a high stiffness and strength but was also brittle, shown in Figure 3(a) as red. The high stiffness and strength stem from the inter-fiber crosslinking from PA/GA treatment. The treatment mechanism was carefully studied by FTIR and TEM. The NMP-pre-soaked Kevlar/PA/GA, as described in 2.2, was used as a hard phase in the nanocomposite system.

#### 3.2 (NMP-Kevlar/PA/GA)(PAA/PU/PAA)

The hard (NMP-Kevlar/PA/GA) phase was implemented with soft layers to create a hierarchical structure. Polyurethane (PU) and poly (acrylic acid) (PAA) LBL films studied in our group demonstrated highly ductile behavior of the PU/PAA system [8]. Thus, PU/PAA was chosen to be a soft phase material bonding with Kevlar/PA/GA, which helps to deflect crack propagation in the nanocomposite and prevents catastrophic failure of the brittle Kevlar/PA/GA phase. One hierarchical film was made in this way: after obtaining 25 layers of Kevlar/PA/GA, the films were sequentially dipped in PU, PAA and PU solutions to get a thin layer of PU/PAA/PU on one surface of the Kevlar/PA/GA film. Four films of this were hot pressed under pressure of ~30MPa at 230 °F for 30 minutes to bond the films (Figure 4b). This layered structure provided enhanced ductility and thus improved the sample toughness.



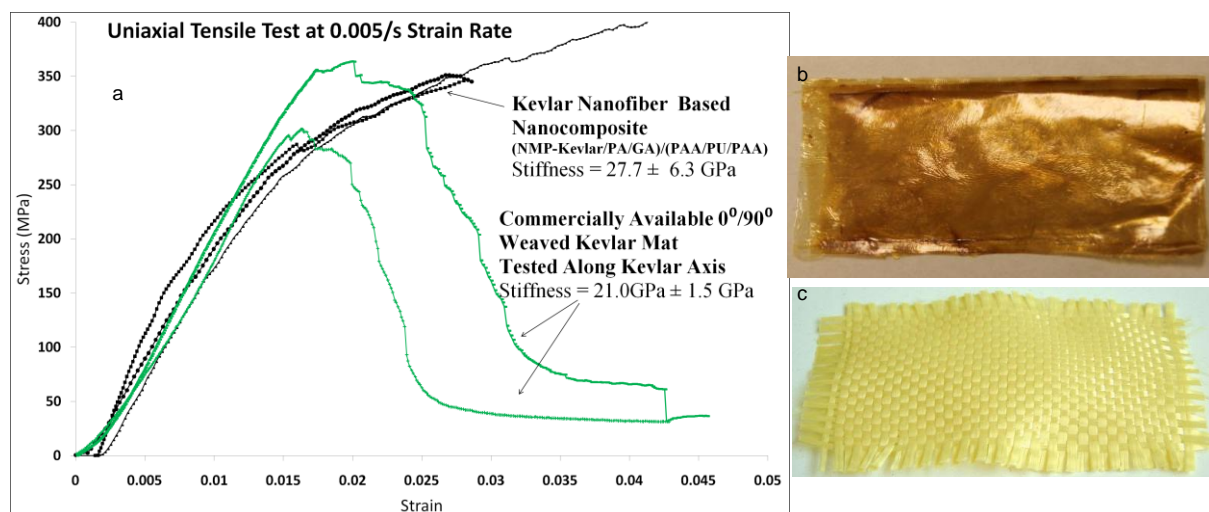
**Figure 3.** a) Stress-strain curves of hard Kevlar phase with PA/GA treatment (Kevlar Nanofiber LBL Assembled Network) and four hierarchically structured Kevlar samples with different loadings of Kevlar hard phase (Kevlar/PU/PAA). b) Schematic showing the layered structure in Kevlar/PU/PAA samples.



**Figure 4.** TGA curves of hard Kevlar phase (Kevlar/PA/GA), four hierarchical Kevlar samples with different loadings of Kevlar hard phase, as well as Kevlar LBL with no PA/GA treatment and PU/PAA for comparison. The color of each film is the same as the one in their corresponding stress-strain plot (Figure 3). The stiffness of the hierarchical samples varied accordingly to the amount of Kevlar in the samples.

### 3.3 Kevlar-based nanocomposite and commercial Kevlar mat

When the PAA/PU/PAA layer was thin, the stiffness and strength of the hard Kevlar/PA/GA phase were preserved and PU/PAA layers were used as a crack deflect layer to improve toughness. Such a Kevlar-based nanocomposite had higher stiffness and strength compared to those of the commercial Kevlar mat tested along its strongest axis (Figure 5).



**Figure 5.** a) Stress-strain curves of Kevlar nanofiber based nanocomposite (NMP-Kevlar PA/GA)/(PAA/PU/PAA) (b) and commercial Kevlar woven mat (c) .

## 4 Conclusions

A Kevlar-based nanocomposite comprised of alternating layers of hard Kevlar/PA/GA (phosphoric acid and glutaraldehyde treated Kevlar) phase and soft PU/PAA/PU (Polyurethane/Poly (acrylic acid)/Polyurethane) phase was demonstrated to have higher stiffness and strength than those of commercial Kevlar fiber woven mats tested along their strongest axis. A high stiffness and strength, but relatively brittle Kevlar/PA/GA layer was obtained by assembling Kevlar nanofibers with PA/GA surface treatment. Commercial Kevlar yarns were dispersed as nanofibers with diameter between 3 and 30 nm and used as nanoscale building blocks which were assembled via LBL or filtration methods into transversely isotropic thin films. PA/GA treatment was implemented to enhance the interactions between

the nanofibers by creating functional groups on nanofiber surfaces through PA hydrolysis and inter-fiber GA crosslinking. PU/PAA was used as ductile layers bonded between the hard Kevlar/PA/GA to improve toughness. When thin layers of PU/PAA/PU were implemented, the high stiffness and strength of the hard Kevlar/PA/GA phase were maintained, while PU/PAA/PU served effectively as weak interphase for crack deflection.

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